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The properties and theory of genesis of the carbonaceous complex within the cold bokevelt meteorite

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(*Received* 4 *December* 1952)

ABSTRACT

The carbonaceous substances within the Cold Bokevelt Meteorite and other similar types of stones show uniform distribution. The Cold Bokevelt carbonaceous stone proved to contain over 1% extractable organic substances. The results of analyses, de-ashing experiments, etc., indicate that in addition the stone may bear a considerably higher proportion of carbonaceous matter. The extracts consist mainly of complex organic acids, they contain some organic chlorine, an element which has not been so far detected within any of the terrestrial bitumens. The fact that the extracts are optically neutral indicates that the organic matter may have been condensed from the atmosphere of the parent body through non-biological processes of polymerisation, etc. The low decomposition temperature of the finely divided carbonaceous substances seems to point to the hypothesis that the meteorite in question must have condensed under low-temperature conditions.

Introduction

Organic substances in meteorites were reported long ago, especially from 1835 to 1885; abstracts of most of the old references are given in the book of E. Cohen (1894). Claims were made that substances had been extracted with ether and alcohol from the following stones: Allais, Carcote, Cold Bokevelt, Collescipoli, Kaba, Meghei and Nagaya. Orgueil and Goalpara were recorded as yielding small quantities of carbonaceous residues after the elimination of silicates with acids. In addition, there are eleven other meteorites, in which the presence of organic substances was claimed on less positive grounds, such as dark grey coloration, odour on heating, etc. The old literature does not refer to the composition, structure or problems of origin of the carbonaceous matter within the meteorites, and the present research was undertaken in order to investigate these interesting questions.

Experimental Work

In the collections of the British Museum there are samples from each of the twenty "carbonaceous" meteorites, referred to above. The stones are all chondrites with very little or no metal. Compared with the average chondrite, the majority are unusually loose in texture, particularly those stones, all without metal, in which the presence of organic substances was established by previous workers using reasonably reliable methods.

Under the binocular microscope, all the stones show uniform, light to dark grey coloration beneath a somewhat darker surface crust, the shade being the same throughout any specimen and even in different stones of the same shower. Thin sections invariably reveal "bituminous" substances, concentrated within the turbid, amorphous ground mass cementing the light coloured chondrules and the occasional phenocrysts. No discrete carbonaceous particles can be resolved

in the matrix even under the highest powers of magnification. The stones show as a rule no fluorescence in ultra-violet radiation. This fact is held to indicate the absence of free hydrocarbons, with a hydrogen-carbon ratio over 1·4, as such bitumens from terrestrial sources invariably fluoresce. The only exception is a faint brown luminescence in the surface crust of the Kaba meteorite, and indeed this cannot be resolved into discrete fluorescent particles with the microscope. It is interesting to note that this was the only stone from which ether extracts of vaselinous consistency were recorded (F. Wöhler (1859) and W. Hardinger (1859)). The extracts from the other meteorites were said to be more or less resinous.

In the course of research work during 1951–52 the hydrocarbons within the Cold Bokevelt meteorite were investigated in some detail, although the alcohol extracts of this stone had already been briefly described by F. Wohler and W. Hardinger (1859).

For purposes of organic microanalysis a small sample of the meteorite without surface crust was ground and treated with dilute hydrochloric acid in order to expel CO_2 from any carbonates, but no trace of carbonate could be detected. The sample was dried for 48 hours over calcium chloride at ordinary pressure, and on analysis was found to contain

C:	2·20%
H:	1·53%
S:	1·99%
O, etc.:	4·84%
Residue:	89·44%

An X-ray examination of the partly de-ashed substance of the meteorite produced no evidence of graphite (see below), so it is likely that the whole of the carbon found originates from the hydrocarbon. Part of the H and O on the other hand might have been produced from the decomposition of hydrated silicates. The results of extraction indicate that a small proportion of the S was present in the elemental state; iron sulphide was not detected with the microscope.

In order to separate the carbonaceous substances, 12 g of finely-ground powder of the meteorite was treated with a mixture consisting of equal parts of concentrated HCl, HF, and water. After two weeks' digestion at room temperature the residue still contained over 60% of silicates. Subsequently the same sample was placed in a similar acid mixture for three months and then heated on a water bath for 100 hours. The insoluble residue was reduced by this further treatment to approximately 30%. It should be stressed that, under similar treatment, the insoluble residue of shales would have been reduced well below 2%. The difficulty experienced in the "de-ashing" of the meteorite might be due to the fine grains of silicates being coated with a protecting sheath of carbonaceous matter (see p. 7).

It was this impure, partially "de-ashed" residue, whose X-ray powder diagram showed no lines of the graphite pattern.

A 20·0 g sample of the powdered meteorite was distilled and the products of distillation condensed at −50°C. The temperatures given on the left in the table

were measured at the neck of the flask, and it seems from the thermal decomposition of another small sample (see below), that the substance overheats to a considerable extent during distillation. The following fractions were separated:

95–105°C:	0·783 g (3·93%)	Water with a slight trace of finely divided sulphur.
105–200°C:	1·584 g (7·42%)	Water with 0·0086 g (0·043%) sulphur, coloured dark brown by a trace of carbonaceous substances.
200–500°C:	0·521 g (2·60%)	Water with 0·0042 g (0·21%) sulphur, coloured black with traces of carbonaceous substances.
Loss:	0·461 g (2·30%)	Inflammable gases, not analyzed.
Residue:	16·638 g (83·190%)	

The watery fractions had an aromatic, rather spicy odour, different from that of the distillation products of terrestrial bitumens. The meteoritic powder became considerably darker—nearly black—during heating.

After the distillation the residue was placed in a vessel over water in order to determine the percentage of moisture which could be reabsorbed, with the following results:

	Residue: wt. in g		%
After heating to 500°C:	16·638	Loss:	16·810
After 1 day standing:	16·775	Regained:	0·685
After 2 days standing:	16·889	Regained:	1·265
After 5 days standing:	16·953	Regained:	1·575
After 10 days standing:	17·061	Regained:	2·115
After 20 days standing:	17·064	Regained:	2·130
After 30 days standing:	17·066	Regained:	2·140
After 40 days standing:	17·067	Regained:	2·145
After 50 days standing:	17·067	Regained:	2·145
After 100 days standing:	17·067	Regained:	2·145
After 250 days standing:	17·067	Regained:	2·145

The above results show that of the total of 13·95% water lost during heating of the meteorite powder to 500°C, only 2·15% were re-absorbed at room temperature in a saturated atmosphere. Hence it seems that the bulk of the water was chemically attached to the carbonaceous complex and the hydrated silicates within the meteorite. It is most unlikely, therefore, that the water content of the meteorite would be of terrestrial origin, especially as the introduction of over 10% moisture into the molecules constituting the stone would have certainly caused some visible signs of chemical alteration, and most likely a complete decomposition to powder.

The thermal decomposition of a small powdered sample of the meteorite was determined by maintaining it for 5 hours at a time at temperatures ranging from 50 to 350°C.

Temp. °C	*Weight* g	*Loss* g	*Loss per cent*
—	0·1382	—	—
50	0·1382	0·0000	0·00
75	0·1380	0·0002	0·15
100	0·1379	0·0003	0·22
125	0·1376	0·0006	0·43
150	0·1371	0·0011	0·80
175	0·1369	0·0013	0·94
200	0·1366	0·0016	1·16
225	0·1361	0·0021	1·52
250	0·1357	0·0024	1·73
300	0·1350	0·0032	2·32
350	0·1268	0·0114	8·25

After heating to red heat the residue weighed 0·1160 g, the total loss being 16·05%. This is slightly less than the loss of 16·81% by the distillation of the larger sample in a closed vessel, possibly because, during the prolonged heating of the small sample in an open crucible, some oxygen may have combined with the ferrous iron.

12·5 g of finely-powdered meteorite was extracted for 8 hours each at the boiling point, with the following solvents; methyl alcohol, ethyl alcohol, chloroform, benzene and carbon disulphide. It was found that a more prolonged extraction with a given solvent removed only slight additional traces of organic substances. The extractions for 8 hours at the boiling points of solvents yielded:

Methyl alcohol:	0·508%
Ethyl alcohol:	0·204%
Chloroform:	0·160%
Benzene:	0·242%
Carbon disulphide:	0·002%
Total:	1·116%

Another sample of 10·0 g, was extracted under identical conditions with the same solvents except carbon disulphide, in the reverse order:

Benzene:	0·655%
Chloroform:	0·017%
Ethyl alcohol:	0·424%
Methyl alcohol:	0·029%
Total:	1·125%

From the results ethyl alcohol and benzene were evidently the best extracting agents.

The extracts were insoluble in water, but soluble in all the organic solvents. All had an identical, rather aromatic, spicy smell. There were slight differences however in colour and fluorescence: the benzene extracts had a dark brown colour and brown fluorescence, the extracts with other solvents were of light brown colour and greenish-yellow fluorescence. The consistency was soft and resinous, extracts with chloroform being particularly soft, almost semi-liquid. None of the extracts was attacked by acids; with alkalies they formed brown solutions, with precipitation of some iron oxide.

The extracts were subsequently mixed and re-precipitated from alcohol. Some sulphur crystals, representing 10 to 12% of the total weight were eliminated by hand picking. Analyses of the remainder yielded:

C:	19·84%	24·26%	excluding ash
H:	6·64%	8·12%	,, ,,
N:	3·18%	4·00%	,, ,,
S:	7·18%	8·78%	,, ,,
Cl:	4·81%	5·89%	,, ,,
O, etc.:	40·02%	48·95%	,, ,,
Ash:	18·33%		
	100·00%	100·00%	

The halogen found was calculated as chlorine, because this would be presumably the dominant element present from the Cl-Br-I group. The presence of halogen is of considerable theoretical interest, since no elements of this group have so far been recorded from any of the terrestrial bitumens. A 0·02 g sample of the extracts was treated with an acid solution of silver nitrate, in order to determine any halogen which might have been extracted by the solvents in the form of inorganic salts. At room temperature no trace of precipitate could be detected, and after 15 minutes boiling there was only a very slight turbidity in the silver nitrate solution, which could have been caused by some of the organic halogen derivatives, decomposing spontaneously. Thus the above experiment indicates that certainly the bulk of the halogen in the extracts was organic.

The thermal decomposition of the extracts was measured by heating a small sample for 5 hours to temperatures ranging from 100 to 350°C:

Temp. °C	*Weight* g	*Loss* g	*Loss per cent*
—	0·00510	—	—
100	0·00475	0·00035	6·9
125	0·00440	0·00070	13·7
150	0·00420	0·00090	17·6
175	0·00385	0·00125	24·5
200	0·00315	0·00195	38·2
225	0·00260	0·00250	49·0
250	0·00245	0·00265	52·0
300	0·00240	0·00270	52·9
350	0·00230	0·00280	54·9

The residue was black, evidently containing carbon, and after ignition it left a brown ash. It is interesting to note that the extracts of the meteorite lost weight at a faster rate, at relatively low temperatures, than the powdered stone, possibly because the decomposition temperature of the hydrated silicates was higher than that of the carbonaceous complex, particularly its extractable portions.

From another portion of the extracts a benzene solution was made in order to determine the optical rotation. The optical rotation of a 5-cm column of 5% solution proved to be below the sensitivity of the instrument, that is less than 0·02°.

The residue of the second extraction was treated with a large excess of concentrated $H_2SO_4 + HNO_3$ mixture in order to nitrate any highly polymerized aromatic bodies in the complex carbonaceous substances, and make these extractable. The residue was filtered after dilution and neutralization and extracted with benzene and nitrobenzene. The solvents extracted 0·006 g and 0·011 g respectively. The extracts were dark brown, and insoluble in alcohol. Further investigation was precluded by the small quantity of the substances.

Theoretical Considerations

1. *Structure of the carbonaceous complex*

The finely divided carbonaceous complex within the ground mass of the Cold Bokevelt meteorite differs in two fundamental aspects from bituminous substances of the terrestrial sedimentary rocks. (1) On distillation, whereas the meteorite yields only water, most of the shales, etc., produce traces at least of liquid hydrocarbons, mainly paraffinic. (2) The carbonaceous rocks of terrestrial origin are not extractable as a rule with solvents, whereas the meteorite yields well over 1% of chlorinated resinous extracts. For the latter reason the term "retigen" is suggested for the carbonaceous complex of the Cold Bokevelt meteorite in contrast to the "kerogen" of shales. The extracts of the carbonaceous complex might be termed "chlorobitumens."

The high over-all percentage of oxygen in the extracts, and presumably in the whole carbonaceous complex, seems to account for the absence of liquid hydrocarbon fractions, for these would tend to decompose to water and carbon.

The good alkali solubility and the bulk composition of the extracts suggest that these are essentially complex organic acids with some substituted N, S and halogen; and possibly with small quantities of other elements that have not been so far detected. The terrestrial hydrocarbon mineral which the extracts most closely resembles is dopplerite, a calcium salt of humic acids. It is true that no water-extractable inorganic salts could be detected in the extracts of the meteoric hydrocarbon; a high percentage of the acid radicals seems to form salts with the iron and possibly other metals, and these are left behind in the ashes after ignition.

The original carbonaceous complex may be of a structure mainly similar to that of its extractable portions, though richer in carbon and possibly containing some free amorphous C as well.

The extracts by the various solvents all seem to be heterogeneous; that is, they contain substances of differing solubility, some of which fall out as flakes from relatively concentrated solutions, whereas others leave a film after the complete

evaporation of the solvent. There can be little doubt, particularly if we consider experience with terrestrial hydrocarbons, that both the original carbonaceous complex and its extracts contain a considerable variety of molecules of complicated structure, though the bulk of these belong to the above mentioned acidic type. It is unlikely that sufficient material would be available from any of the carbonaceous meteorites for an attempt to separate and identify some of the substances, but it is conceivable that infra-red and ultra-violet spectroscopy, X-ray analysis, determination of saponification value, and application of other organic chemical methods on somewhat larger amounts of the organic substance, might yield most interesting information concerning the proportion of radicals and the main types of molecules present. Complete analyses of the carbonaceous and inorganic phases of meteorites would give us the proportions of each element between these.

The organic constituents are likely to contain the residues of the more volatile elements (with exception of the inert gases), the bulk of which would escape during the condensation of the meteoritic substance. Hence their compositions would give us valuable data for the computation of the relative abundance of elements within the universe. Thus, for example, the high proportions of S, Cl, and particularly N, in the extracts of the Cold Bokevelt meteorite suggest that these elements must have been present in still higher proportions in the original substance from which the meteorite condensed. It should be stressed, however, that the affinity for carbon of a volatile element would also help to determine its proportion in the organic complex.

2. *Problem of genesis of the carbonaceous complex*

Regarding the problem of genesis of the carbonaceous substances in meteorites, only brief and tentative suggestions can be found in the literature.

P. E. Spielmann (1924) put forward a theory of formation of the hydrocarbons through hydrolysis of carbides, originally in the meteorites, by terrestrial water. This hypothesis should be discarded for the same reasons as the suggestion of a terrestrial origin for the water content (see p. 2). In order to produce over 1% extractable hydrocarbons, i.e. possibly from 3 to 5% of carbonaceous matter, a minimum of 15 to 25% of carbides would be necessary. The decomposition of such a high proportion of the stone would most certainly cause crumbling to powder, or at least the appearance of iron oxide stains, and these cannot be seen anywhere in the stone, notwithstanding its general uniformity.

It is often implied in popular works that the presence of organic substances in meteorites would indicate the existence of life on the celestial body of their origin. However, the extracts from the Cold Bokevelt meteorite proved to have no measurable optical rotation, and this fact must be held to indicate a non-biological origin. The earth's biologically formed carbonaceous minerals, such as oils, or retorting products of coals, etc., invariably show optical rotation.

In the light of modern organic chemical experience, there seems to be no great difficulty in accounting for a non-biological origin of the organic substances. The existence of CH, CN, and similar radicals in atmospheres of comets has been proved spectroscopically. It is reasonable to conjecture that under conditions of varying illumination and temperature a proportion of the constituents of such an

atmosphere would polymerize into complex molecules. These in turn might be collected on the fine dust particles, which may be expected to float through the atmosphere of any relatively small celestial body, and eventually settle on its surface. If the matrix of the Cold Bokevelt meteorite contains extremely small dust particles coated with hydrocarbons, this might possibly explain the difficulties experienced in its de-ashing.

The strikingly high oxygen percentage of the extracts, when compared with that of the average terrestrial hydrocarbons, might be connected with their non-biological origin. On the surface of the earth the green plants convert carbon dioxide into organic molecules of relatively lower percentage of oxygen and free oxygen through the process of photosynthesis. The plant and animal debris is further deoxygenated through micro-organisms and the physico-chemical processes of sedimentation. Without the activity of green plants and micro-organisms however, the initial deoxygenation does not take place, leaving the organic molecules richer in oxygen. According to general organic chemical experience, these acid substances are as a rule more stable, against loss of oxygen, than terrestrial plant debris that consists mainly of cellulose.

The presence of N, S, and Cl in the extracts implies, if our hypothesis proves to be the correct one, that the primitive atmosphere surrounding the original condensation contained these elements in relatively high proportions. The chlorine might have been present as HCl, when it could have entered the olefinic molecules only, or in elemental form, in which case it would easily displace H atoms from all types of hydrocarbons.

From the above considerations it seems that there may be a distinct similarity between the composition of the carbonaceous complexes on different celestial bodies, whether these are with or without life as we know it here on earth; and the role of organisms in the history of organic substances may not be so fundamental as is generally believed. Under a given set of physical conditions, reasonably similar substances may be formed either through biological or non-biological processes; the presence of bituminous substances of apparently magmatic origin in pegmatite veins seems to support the above suggestion. It would then seem that the most important factors in the formation of complicated organic molecules, in a system containing carbon, are the temperature and pressure of that system.

3. *The use of meteoritic carbonaceous complexes as "natural thermometers"*

Spectroscopic investigation of interstellar space indicates that the elements which readily enter carbon chains, that is O, H, N, S, etc., are present there in elemental form or as simple compounds with carbon. If we consider a condensing body within such a gaseous system of discrete atoms, simple radicals, or molecules, we see that different types of equilibria can develop according to the conditions prevailing in the condensing body. We are led to conclude that the carbonaceous complexes of both terrestrial rocks and meteorites possess considerable value as indicators of temperature and also possibly other physical and chemical conditions prevailing during their formation. This value as indicators is not seriously affected by the presence of living organisms.

Experience from a variety of terrestrial rocks clearly indicates that what may be symbolized as the "C—(H, O, N, S) equilibrium" in any given rock was generally reached when the rock was at the highest temperature in its history, and was as a rule little affected during subsequent epochs at lower temperatures. For example finely divided carbonaceous complexes that decompose in the range 100 to 500°C have been recorded so far only in sedimentary rocks. In the slightly metamorphosed slates, on the other hand, graphite is the only form of carbon that has been so far found. The metamorphism of carbonaceous sediments needs more careful study than it has yet received, but the incomplete data at present available suggest that carbonaceous substances yielding more than a trace of volatiles are absent from all the metamorphic rocks. Nor have finely divided hydrocarbons been recorded in the igneous rocks though, as previously mentioned, bituminous substances of magmatic origin are found in numerous pegmatite veins, which traverse igneous rocks. While studying the alteration of hydrocarbons by mineralizing solutions that has occurred in Derbyshire, I recently found that the bitumens are of relatively higher initial boiling points in those veins, which are believed to have been formed at a relatively higher temperature, on grounds of their high fluorite and low calcite percentage. Thus it seems, that the system C (H, O, N, S) can be used as a "natural thermometer" with reasonable confidence, at least as a first approximation.

We can now consider the Cold Bokevelt meteorite, with its carbonaceous complex of low decomposition temperature, and with over 1% its total mass extractable by organic solvents. The implication is that this meteorite (and possibly others of similar properties) was formed at a low temperature, and never reached a high temperature after this first consolidation. From the table of decomposition of extracts it seems likely that the temperature did not exceed 200–350°C, providing the pressure was relatively low. Even under a very high pressure, however (which seems to be rather unlikely in view of most theories of the formation of meteorites), the temperature could not have risen as high as 600°C, for the complex molecules of high percentage of oxygen would then have decomposed, whatever the pressure.

Other chondrites and all the achondrites are likely, to judge from available records, to contain amorphous carbon, and on heating they give off gases, dominated as a rule by methane and carbon monoxide. Published data do not seem to rule out the presence of small quantities of carbonaceous substances of very low volatile proportion. This type of C—(H, O, N, S) equilibrium would put the maximal values of temperature throughout the history of the stones say between 500 and 1200°C.

Finally, the iron and stony iron meteorites rich in metal often contain graphite and yield mainly hydrogen on being heated. These are indications that they have had a high temperature epoch of over 1000°C during or after their condensation.

The above considerations suggest, then, that the carbonaceous chondrites are not igneous melts, but products of condensation at low temperature. The most likely supposition is that they originated as a mass of compacted fine dust, in which the chondrules and occasional phenocrysts were embedded. Neither the chondrules nor the phenocrysts appear to contain carbonaceous substances,

confirming the conclusions of independent mineralogical investigations, that both kinds of inclusion solidified at relatively high temperatures, presumably from melts. Thus the carbonaceous meteorites are fragmental aggregates.

By analogy it would seem that the "non-carbonaceous" chondrites and the achondrites condensed at a higher temperature, permitting the partial fusion of their dust particles, and hence their usually much firmer structure. It is interesting to note, in this connection, that G. P. Merrill (1921) postulated a tuff structure for the chondrites on petrological grounds.

By this study of carbonaceous complexes we seem to have found a clue to the approximate maximum temperature prevailing during and after the consolidation of a particular type of meteorite. This consideration should now be applied to all the general theories on the origin of meteorites, but a critical survey of hypotheses of meteorite formation in the light of the results of research on the carbonaceous complexes is outside the scope of the present paper.

I would like to thank Dr. W. Campbell Smith of the British Museum (Natural History), London, for his encouragement and kindness in placing at my disposal parts of the Cold Bokevelt Meteorite, and also Dr. M. H. Hey of the British Museum for providing facilities for the chemical work. Finally, I would like to convey my deep appreciation to Professors S. E. Hollingworth and E. P. Hughes of University College London, and Professor H. C. Urey, For. Mem. R.S., of University of Chicago of their constructive and highly encouraging criticism.

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Argonbestimmungen an Kalium-Mineralien

II. Das Alter eines Kalilagers im Unteren Oligozän

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ABSTRACT

New measurements of the argon-content in potassium salts are reported. The results indicate a relationship between the argon-content and the size of the crystals investigated. By comparison of the experimental data with theoretical calculations, a diffusion constant of $(1{\cdot}5 \pm 1) \times 10^{-19}$cm^2/sec for argon in potassium chloride can be found. Considering these results the measurements lead to an age of $(21 \pm 3) \times 10^6 a$ for the lower oligocene, the geological period from which the examined samples come. The geological influences that could have been able to alter the given value of the age, and the magnitude of the possible error are discussed.

Einleitung

In einer früheren Arbeit berichteten wir (Smits und Gentner, 1950) über Bestimmungen des Kalium-Argon-Verhältnisses an tertiären Kalisalzen. Es hatte sich danach gezeigt, daß an verschiedenen Proben des gleichen Lagers kein einheitlicher Wert erhalten werden konnte. Über die Ursachen dieses offensichtlich eingetretenen Argonverlustes konnten nur Vermutungen ausgesprochen werden. Die vorliegende Arbeit läßt diesen Argonverlust verstehen und ihn im Sinne einer Diffusion quantitativ erfassen. Es kann daher jetzt ein Alterswert für das Kalilager mit wesentlich größerer Sicherheit angegeben werden.

Eine weitere Unsicherheit bildete seinerzeit das genaue Zerfallsschema des Kalium 40. Mehrere Arbeiten von anderer Seite (vgl. Houtermans *et al.*, 1950) bestätigten das von uns angenommene Zerfallsschema. Es darf daher heute mit Sicherheit angenommen werden, daß jeder K-Übergang des Kalium 40 mit einem γ-Quant gekoppelt ist. Für die Ermittlung der Zerfallskonstante für den K-Einfang ist daher die Kenntnis der genauen Zahl der γ-Quanten pro Gramm Kalium und Sekunde wesentlich. Die Messungen für diesen Wert schwanken in der neueren Literatur noch zwischen 3,0 und 3,6 (Houtermans *et al.*, 1950; Spiers, 1950; Faust, 1950; Sawyer und Wiedenbeck, 1949 und 1950). Bei der Berechnung des Alterswertes benutzen wir daher jetzt einen mittleren Wert von $3{,}3 \pm 0{,}3$ K-Übergängen pro Gramm Kalium und Sekunde, der mit seiner Fehlergrenze die besten neueren Messungen einschließt.

Abtrennung des Argons

Die Bestimmung des Argongehaltes ist im wesentlichen in unserer früheren Veröffentlichung beschrieben (Smits und Gentner, 1950). Da zunächst der Verdacht vorlag, daß die beobachteten Unterschiede im Argongehalt im Meßvorgang bedingt sind, wurde die Methodik verbessert. Es zeigte sich, daß der Calcium-Ofen Wasserstoff nur unter nicht reproduzierbaren Bedingungen abbindet. Um diese Unsicherheit auszuschalten, wurde zusätzlich ein Kupfer-Kupferoxyd-Ofen und Phosphorpentoxyd verwendet. Im Kupfer-Kupferoxyd-Ofen, welcher auf ca. 400°C gehalten wird, verbrennt Wasserstoff unter Reduktion

des Kupferoxyds zu Wasser, das anschließend vom Phosphorpentoxyd aufgenommen wird. Ferner adsorbieren wir vor der endgültigen Mengenbestimmung zunächst das Argon in Aktiv-Kohle bei der Temperatur der flüssigen Luft. Sodann wird in mehreren Schritten das restliche Argon aus der Ausfriertasche entfernt und adsorbiert. Es hat sich nämlich gezeigt, daß bei weitgehend reinem Argon selbst bei nur $-30°C$ noch eine Adsorption in der Ausfriertasche eintreten kann. Nachdem man sich überzeugt hat, daß kein Gas mehr in der Ausfriertasche

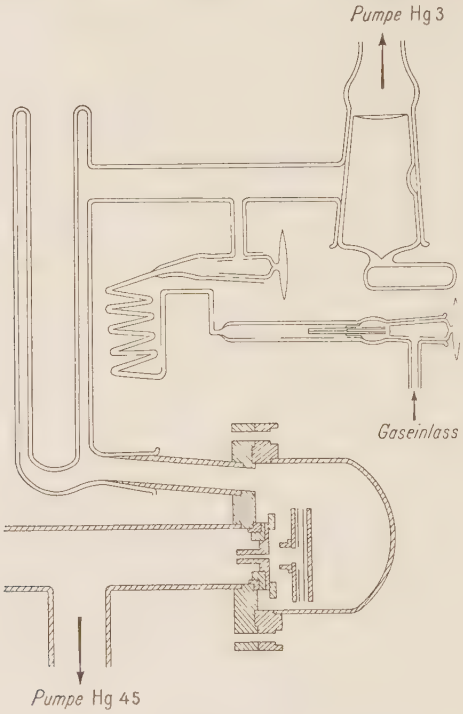

Abb. 1. Ionenquelle mit Gaszuleitung

nachweisbar ist, erfolgt die Desorption des Argons mit anschließender Nachreinigung durch den Calcium-Ofen und die Mengenbestimmung. Es wurde kontrolliert, daß bei Zimmertemperatur Argon wieder quantitativ aus der Aktiv-Kohle desorbiert.

Es lassen sich so bei den üblichen Gasmengen sicher Genauigkeiten von 5% erzielen. Bei sehr kleinen Gasmengen muß mit einem absoluten Fehler von $\pm 0{,}2$ mm³ gerechnet werden.

Massenspektrometrische Prüfung

Zur Bestimmung des Luftargongehaltes wird, wie bereits berichtet (Smits und Gentner, 1950; Pahl *et al.*, 1950), der Gehalt an A^{36} bestimmt. Speziell zu diesem Zweck haben wir ein neues Massenspektrometer gebaut. Dieses muß bei möglichst kleinem Gasverbrauch noch ausreichende Ströme liefern, um Isotopenverhältnisse

von $1 : 10^4$ messen zu können. Mit diesen Anforderungen lassen sich noch Luftverunreinigungen von 3% erkennen.

Die Ionenquelle des 60°—Massenspektrometers zeigt Abb. 1. Zwischen dem Ionenquellenraum und dem Ionenrohr liegt eine scharfe Strömungsbremse in Form eines Kanals $0{,}3 \times 3 \times 20$ mm. Die Gaszuleitung führt über eine Kapillare und eine mit flüssiger Luft gekühlte Spirale zur Ionenquelle. Die Ausfriervorrichtung an der Quelle dient zur Herabsetzung des Störuntergrundes (Kohlenwasserstoffe auf allen Massen), der bei den schwachen Ionenströmen der Linie 36 stark ins Gewicht fällt. Diese Anordnung ermöglicht es, daß mit einigen mm^3 Gas ein Druck von 10^{-4} Torr über längere Zeit in der Ionenquelle gehalten werden kann. Bei diesem Druck sind die Ionenströme groß genug, um den Nachweisverstärker auf der Linie 40 voll auszusteuern. Läßt man einen zeitlichen Abfall der Intensität zu, so kann noch mit 0,1 mm^3 Gas gemessen werden. Die Halbwertszeit des Druckabfalles beträgt dann etwa 2,5 min. Bei voller Aussteuerung des Verstärkers ist die Linie 40 jedoch sehr stark zu kleineren Massen verbreitert, sodaß die Linie 36 nur schwer getrennt werden kann. Durch eine Gegenfeldanordnung wird die Auflösung wesentlich verbessert. Das Ionenrohr liegt dabei auf Hochspannung und der Auffänger auf Erdpotential. Die Ionen müssen so die Beschleunigungsspannung entgegengesetzt durchlaufen, wobei verlangsamte Ionen den Auffänger nicht erreichen können.

Die Ionenquelle selbst entspricht etwa der von PLOCH (1951) beschriebenen. Als Nachweisverstärker wird ein Elektrometerverstärker mit Galvanometer benutzt. Der Gitterableitwiderstand der Meßröhre T 114 beträgt 10^{11} Ohm. Die Nachweisgrenze liegt bei 5×10^{-16} A. Als Ablenkmagnet dient ein Elektromagnet mit röhrenstabilisiertem Netzgerät, ähnlich wie bei PHILBERT (1952) beschrieben.

Bei den Messungen wurden abwechselnd die Linien 40 und 36 ausgemessen. Nachträglich wurde bei unveränderter Ionenquelle die Störintensität auf der Masse 36 bestimmt und als Korrektur abgezogen. Die halbe Höhe der Störlinie wurde als zusätzlicher Fehler behandelt, da es nicht sicher ist, ob die Störlinie als reine additive Konstante in Rechnung gebracht werden darf.

Die so erhaltenen Werte für den Gehalt an A^{36} im Vergleich mit den an Luftargon gefundenen Werten ergeben den prozentualen Gehalt an Luftargon. Für Luftargon finden wir $A^{36} : A^{40} = (3{,}58 \pm 0{,}1) \times 10^{-3}$. Dieses Verhältnis liegt etwas höher als der von NIER (1950) angegebene Wert $3{,}38 \times 10^{-3}$. Bei der Bestimmung des Luftargongehaltes der untersuchten Proben spielt diese Diskrepanz jedoch keine Rolle.

Messergebnisse

Untersucht wurden neben den Salzen des Kaliwerkes Buggingen, die wir früher bereits beschrieben haben (SMITS und GENTNER, 1950), auch Salze der im Elsaß liegenden Grube Anna. Das dort im Wittelsheimer Becken abgebaute Salz hat geologisch den gleichen Ursprung. Das Profil zeigt einen gleichen Aufbau wie in Buggingen, die einzelnen Schichten konnten einander zugeordnet werden.

Die Ergebnisse der Messungen sind in Tabelle 1 zusammengestellt. Bei den meisten Messungen wurden noch mehrere Proben gemeinsam massenspektrometrisch untersucht, da erst im Verlauf der Untersuchungen das Massenspektrometer zur notwendigen Empfindlichkeit hochgezüchtet wurde.

Die bereits in der früheren Arbeit beobachtete Streuung der Meßwerte bestätigte sich. Zur Veranschaulichung sind in Abb. 2 die früheren und die hier vorliegenden Meßergebnisse graphisch nach steigendem Argongehalt geordnet. Bei dieser Art der Darstellung und dem jetzt reichhaltigeren Material erkennt man, daß damit die Schichten auch nach steigender Kristallgröße geordnet sind.

Tabelle 1

Nr.	*Probe*	mm^3A	*g K*	mm^3A	*g K*	% *Luftargon*	$\frac{mm^3 rad.A^{40}}{100\ g\ K}$
61	Ei Bugg.	5,42	70				
62	Ek Bugg.	5,25	76	19,33			
63	Ek Bugg.	4,55	70,5	±2,0	286,5	14,25 ± 1,7	5,80 ± 0,8
96	Ek Bugg.	4,11	70,0				
64	Bh Bugg.	2,40	49				
65	Bh Bugg.	2,26	47,5	10,08	210,5	29,75 ± 2,5	3,37 ± 0,4
66	Bh Bugg.	2,76	57,5	±1,0			
67	Bh Bugg.	2,66	56,5				
68	Bg Els.	5,24	97,5				
69	Bg Els.	5,59	101	20,32	397,0	18,75 ± 1,5	4,16 ± 0,2
70	Bg Els.	4,88	103	±1,0			
71	Bg Els.	4,61	95,5				
76	Bi Els.	5,55	94	16,48			
77	Bi Els.	6,01	86	±1,0	268	23,0 ± 2	4,73 ± 0,2
78	Bi Els.	4,92	88				
79	Ca Els.	4,24	91,5	8,48	183,5	29,5 ± 3	3,25 ± 0,13
80	Ca Els.	4,27	92	±0,2			
81	Bi Els.	6,04	99,5				
82	Bf Els	4,57	86	23,27			
83	Bf Els.	4,66	86,5	±0,4	440,0	16,0 ± 1,2	4,45 ± 0,1
84	Bp Els.	4,24	88,5				
85	Bp Els.	3,76	79,5				
89	Cd Els.	1,85	42,5				
90	Cd Els.	2,04	57	15,92			
91	Ch Els.	4,26	76,5	±0,3	326,5	30,5 ± 2,2	3,39 ± 0,13
92	Cg Els.	3,78	65				
93	Cn Els.	3,99	85,5				
97	Ek Bugg.	4,01	70,5	14,47			
98	Ei Bugg.	4,14	69,5	±0,3	192	24,75 ± 1,5	5,65 ± 0,15
99	Eo Bugg.	6,32	52				
100	Eo Bugg.	3,96	45,5	7,86	92	19,5 ± 2,8	6,90 ± 0,30
101	Eo Bugg.	3,90	46,5	±0,15			
102	Bi Bugg.	6,43	94,5	6,43 ±0,3	94,5	5,5 ± 2,0	6,45 ± 0,4
103	Bi Bugg.	5,82	93,0	5,82	93,0	4,75 ± 1,5	5,95 ± 0,4

Auf dieses wichtige Ergebnis stützen sich unsere weiteren Überlegungen. Ein Zusammenhang zwischen anderen Größen (Beimengungen löslicher und unlöslicher Bestandteile) und dem Argongehalt konnte dagegen nicht gefunden werden.

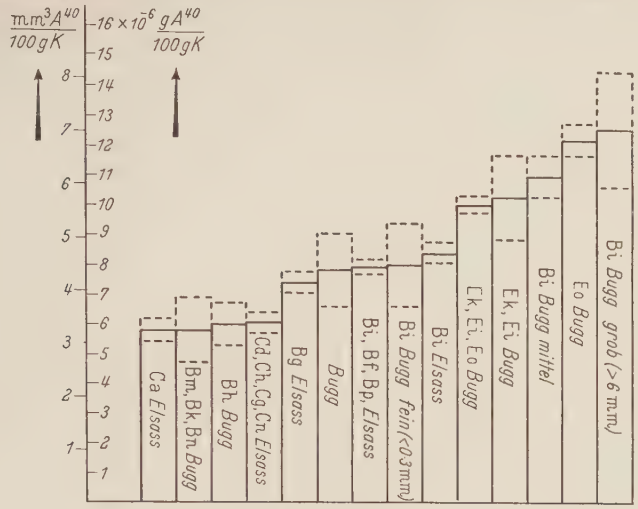

Abb. 2. Argon-Kalium-Verhältnisse verschiedener Schichten

Zur Veranschaulichung der extremen Größenverhältnisse zeigt Abb. 3 zwei Beispiele von Schliffen einer sehr grobkörnigen und einer sehr feinkörnigen Schicht. Durch Auszählen der Kristalle pro Flächeneinheit an derartigen Schliffen wurde für verschiedene Schichten der mittlere Kristalldurchmesser ermittelt, wie er in Tabelle 2 angegeben ist.

Tabelle 2. Kristallgrößen

Schicht	*Kristallgröße d (cm)*
Ca Els.	0,051
Bh Bugg.	0,061
Bf Els.	0,0895
Ei Bugg.	0,129
Ek Bugg.	0,158
Bi Els.	0,255
Bi Bugg.	0,262
Bg Els.	0,271
Eo Bugg.	0,403
	Fehler ca. 10%

Diffusion des Argons in KCl-Kristallen

Die beobachteten Unterschiede im Argongehalt weisen zunächst auf einen mehr oder weniger starken Verlust des Argons in den einzelnen Schichten hin. Der erwähnte Zusammenhang mit der Kristallgröße läßt mit großer Wahrscheinlichkeit eine Diffusion vermuten, was auch dadurch bestärkt wird, daß keine

Möglichkeit zur Erklärung der Unterschiede auf Grund geologischer Ereignisse, die dann die einzelnen Schichten verschieden beeinflußt haben müßten, besteht.

Bei der Diffusion kommt einerseits die Möglichkeit einer Oberflächen-bzw. Korngrenzendiffusion, andererseits einer Volumen-bzw. Kristalldiffusion in Frage. Bei einer reinen Oberflächendiffusion können nur diejenigen Argonatome entweichen, die an einer Korngrenze oder auch an inneren Oberflächen entstehen. Das Argon wird aber gleichmäßig im gesamten Volumen gebildet. Unterschiede von der beobachteten Größe könnten bei reiner Oberflächendiffusion nur dann auftreten, wenn die Zahl der Oberflächenatome eines Kristalles vergleichbar ist mit der Zahl der Atome im Innern eines Kristalles. Das heißt aber, daß die Kristallgröße nur etwa atomare Dimensionen haben könnte. Es muß daher angenommen werden, daß bei den von uns untersuchten Kristallen das Argon aus dem Innern des Kristalls herausdiffundieren kann, und somit eine Volumendiffusion vorliegt.

Der diffundierende Stoff (A^{40}) wird in unserem Fall durch den Zerfall des K^{40} laufend nachgebildet. Der theoretisch zu erwartende Verlauf der Argonkonzentration ergibt sich daher aus einer Überlagerung der zweiten Fickschen Gleichung der Diffusion mit der Zerfallsgleichung.

Das zweite FICKsche Gesetz lautet:

$$\frac{\partial c}{\partial t} = \operatorname{div} D \operatorname{grad} c$$

wobei c die Argonkonzentration und D die Diffusionskonstante bedeutet. Bei den hier auftretenden geringen Konzentrationsunterschieden darf man die Diffusionskonstante als unabhängig von der Konzentration ansehen. Damit vereinfacht sich die Gleichung zu

$$\frac{\partial c}{\partial t} = D \Delta c$$

Die Zerfallsgleichung für den dualen Zerfall lautet:

$$\frac{\partial c}{\partial t} = \lambda_K c_{Ko} - \lambda c$$

wobei c_{Ko} die Konzentration des K^{40} zur Zeit $t = 0$ und λ_K und λ die Zerfallskonstante für den K-Einfang bzw. die Gesamtzerfallskonstante ($\lambda = \lambda_K + \lambda_\beta$) bedeuten. Aus der Überlagerung ergibt sich dann die zu lösende Differentialgleichung zu

$$\frac{\partial c}{\partial t} = D \Delta c - \lambda c + \lambda_K c_{Ko}$$

Diese Differentialgleichung läßt sich durch Reihenentwicklungen lösen. Man erhält so einen Ausdruck für die räumliche Verteilung der Argonkonzentration innerhalb eines Kristalles.* Durch räumliche Mittelung über einen, der Einfachheit halber als kubisch angenommenen, Kristall der Kantenlänge d ergibt sich die zu erwartende Argonkonzentration

$$\bar{c} = c_{Ko} f\left(\frac{D}{d^2}, \lambda_K, \lambda, t\right)$$

wobei f eine dimensionslose Funktion ist.

* Eine ausführliche Behandlung dieser Fragen einschließlich der Lösung der Differentialgleichung wird noch von einem von uns (P) an anderer Stelle gegeben.

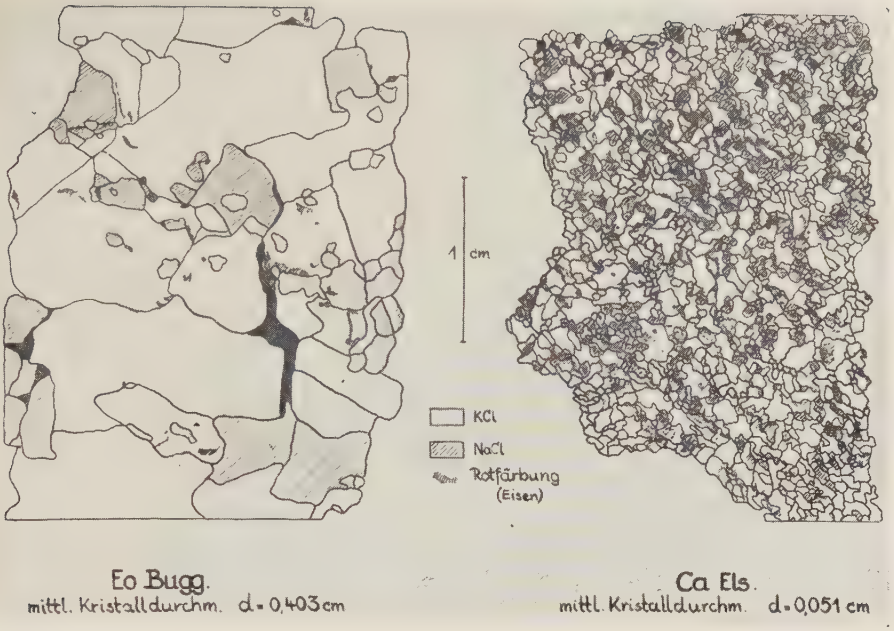

Abb. 3. Schliffe des Kalisalzes zweier Schichten

Abb. 5. Kristalle mit gestörtem Aufbau

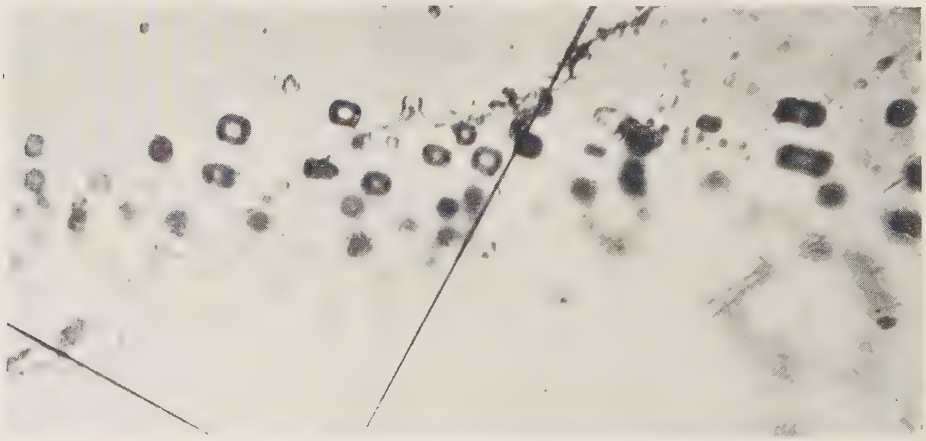

Abb. 6. Störung im Kristallaufbau (ca 500 fach vergr.).

Die numerische Auswertung dieser Funktion gestattet, den Zusammenhang zwischen Kristallgröße (d) und Argongehalt ($\bar{c}$) für verschiedene Werte der Diffusionskonstanten D und verschiedene Zeiten t (Alter) anzugeben. In Abb. 4 sind derartige Kurven eingetragen, die mit den Werten $\lambda_K = 1{,}7 \times 10^{-18}\,\mathrm{sec}^{-1}$ und $\lambda_\beta = 15{,}44 \times 10^{-18}\,\mathrm{sec}^{-1}$ berechnet wurden. Gleichzeitig sind die gemessenen Punkte mit eingezeichnet. Bis auf zwei Punkte, die erheblich aus dem Verlauf herausfallen, lassen sich die Meßpunkte einer einzigen theoretischen Kurve zuordnen. Dabei ist zu erwähnen, daß der Verlauf einer solchen Kurve eindeutig durch Vorgabe zweier Punkte bestimmt ist. Da aber die Meßpunkte bis auf die

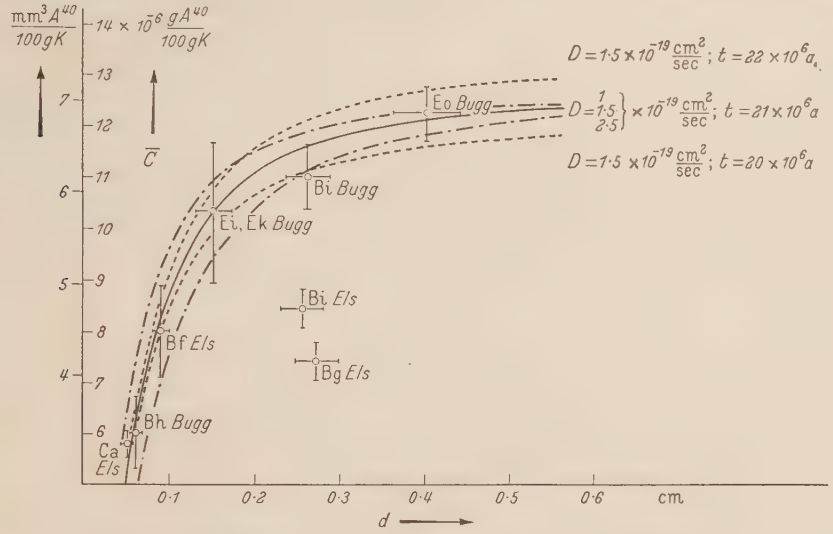

Abb. 4. Abhängigkeit des Argongehaltes von der Kristallgröße

zwei genannten Ausnahmen den gesamten Verlauf der Kurve richtig wiedergeben, kann wohl kein Zweifel darüber bestehen, daß die vorliegende Deutung des Effektes als Volumendiffusion sinnvoll ist.

Bei dem einen der herausfallenden Punkte handelt es sich um die mächtigste Schicht (Bi), die im Lager vorkommt. Diese Schicht weist in sich schon sehr starke Schwankungen in der Kristallgröße und damit auch im Argongehalt auf. Wie man in Abb. 2 sieht, tritt Bi nämlich viermal im Diagramm auf. Eine eindeutige Zuordnung von Argongehalt und Kristallgröße ist daher in diesem Fall nicht möglich. Die Proben für die Argonbestimmung weisen nämlich nicht sicher denselben Kristallaufbau auf wie die Schliffe, da sie nicht immer von genau derselben Stelle stammen. Außerdem ist bei diesem Material (Bi Els.) eine Störung im Kristallaufbau sichtbar, was in noch stärkerem Maße bei der Schicht Bg Els., die als zweiter Punkt herausfällt, zu beobachten ist. Abb. 5 zeigt einen Schliff dieser Schicht. Man sieht innerhalb der einzelnen Kristalle Störungen, die sich als Punktreihen abheben. Unter dem Mikroskop erkennt man, daß es sich um kleine Hohlräume handelt, die in ganzen Ebenen angeordnet sind. Abb. 6 zeigt eine Mikroaufnahme einer derartigen Störung. Durch diese Störungsebenen sind die einzelnen Kristalle mehrfach unterteilt, und es erscheint verständlich,

daß ein zu kleiner Argongehalt vorliegt. Man müßte also diesen Schichten eine kleinere Kristallgröße zuordnen.

Mit der besprochenen Methode läßt sich nun sowohl die Diffusionskonstante des Argons in KCl als auch das Alter der betrachteten Sylvine angeben. Wie man an Hand der eingezeichneten Kurven mit variierter Diffusionskonstante bzw. Zeit leicht verfolgen kann, sind es vornehmlich die kleinkristallinen Schichten, die die Diffusionskonstante bestimmen, während die grobkristallinen Schichten in erster Linie für den Alterswert verantwortlich sind.

Aus den Kurven kann ein Alter $t = (21 \pm 1) \times 10^6 a$ und eine Diffusionskonstante $D = (1{,}5 \pm 1) \times 10^{-19}$ cm²/sec. abgelesen werden.

Berechnet man das Alter aus dem höchsten Argongehalt ohne Berücksichtigung der Diffusion, so ergäbe sich ein Wert, der etwa 20% tiefer läge. Zur Veranschaulichung der Rechnung sei erwähnt, daß sich z.B. bei einem Alter von 15 Mill. Jahren ein Argonverlust von etwa 18% ergibt; bei einem Alter von 35 Mill. Jahren steigt er auf etwa 19%. Dieser geringe Anstieg des Argonverlustes mit dem Alter hängt mit der radioaktiven Nachbildung des Argons zusammen.

Der Fehler des Alters erhöht sich wegen der eingangs erwähnten Unsicherheit in der Zerfallskonstanten um 10%. Es ergibt sich so als Alterswert für das

untere Oligozän: 21 ± 3 Mill. Jahre

Diskussion

Bei dem untersuchten Kalilager handelt es sich um ein Vorkommen, das als Sedimentlager und auf Grund von Pollenanalysen (Kirchheimer, 1950) geologisch eindeutig als unteres Oligozän datiert ist. Der erhaltene Alterswert von 21 Mill. Jahren liegt jedoch niedriger als bisher angenommen wurde. Dazu ist zu sagen, daß für die bisherigen Annahmen lediglich die von Nier (1941) durchgeführte Uran-Blei-Bestimmung an einer laramiden Pechblende (Colorado) einen sicheren Anhaltspunkt bildet. Diese lieferte ein Alter von 60 Mill. Jahren, das geologisch zwischen Anfang oder Ende des Paleozäns datiert wird (Holmes, 1947). Durch eine relative zeitliche Unterteilung des Tertiärs auf Grund entwicklungsgeschichtlicher Tatsachen (vgl. Simpson, 1951) oder der maximalen Sedimentmächtigkeiten in Geosynklinalen (Holmes, 1947) lassen sich dann die Alterswerte der einzelnen Tertiärepochen an obigen Wert anschließen. Diese verschiedenen Methoden ergeben aber nicht übereinstimmende Werte. Es ist auch nicht unbedingt einzusehen, daß der Verlauf der maximalen Sedimentmächtigkeit mit der Zeit eine glatte Funktion ergibt. Die Sedimentationsgeschwindigkeit kann durchaus in den einzelnen Perioden sehr starken Schwankungen unterworfen gewesen sein und sich deshalb trotzdem im Großen dem von Holmes (1947) angegebenen glatten Verlauf annähern. Eine Diskussion dieser Methoden wurde neuerdings von Moore (1952) gegeben. Er weist auch auf die große Unsicherheit derartiger Methoden hin. Für die untere Grenze des Oligozäns werden so Alter bis zu 45 Mill. Jahren angegeben. Zuverlässige Uran-Helium-Bestimmungen aus dieser Zeit liegen andererseits nur an geologisch sehr ungenau datierten Proben vor (Hurley und Goodman, 1941).

Der von uns angegebene Wert könnte nur dann zu niedrig sein, wenn das Lager längere Zeit wesentlich anderen physikalischen Bedingungen unterworfen gewesen

wäre. Wir sehen nur die Möglichkeit, daß einerseits die Temperatur wesentlich höher war, oder daß große Gebirgsdrucke auftraten, die ein Fließen des Sylvins bedingt hätten. Rekristallisationserscheinungen sind aber an den von uns untersuchten Proben nicht zu beobachten, daher muß die zweite Möglichkeit ausgeschlossen werden.

Wenn das Lager tatsächlich eine Zeit lang eine wesentlich höhere Temperatur gehabt hätte, wären unsere Rechnungen nur bedingt anwendbar. Der zeitliche Temperaturverlauf müßte dann für die Auswertung bekannt sein, da die Diffusionskonstante stark von der Temperatur abhängt und eine einfache Mittelwertbildung nicht erlaubt ist. Heute ist die Gesteinstemperatur etwa 38°C. Bei den in Abb. 6 gezeigten Störungen handelt es sich teilweise um Laugeneinschlüsse, die beim Erwärmen des Kristalls auf die Siedetemperatur den Kristall sprengen. Sicherlich ist also das Lager nie über 100°C erhitzt worden.

Den einzigen geologischen Anhaltspunkt für eine eventuelle zeitweilige Temperaturerhöhung bildet ein Ankaratrit-Vorkommen im Lager Buggingen (Hasemann, 1951). An Salzumlagerungen ist zu erkennen, daß die Intrusion mit Wasserdampfentwicklung vor sich gegangen ist. Die Störungen im Salzlager reichen aber nur bis zu 50 m um das Ankaratritvorkommen. Die für die Argon-Bestimmungen benutzten Proben sind aber etwa 2 km von dieser Stelle entfernt entnommen worden. Sollte auf Grund dieser vulkanischen Vorgänge eine lokale wesentliche Temperaturerhöhung eingetreten sein, die das gesamte Bugginger Lager betroffen hätte, so müßten sich an den Bugginger und Elsässischen Salzen grundsätzlich verschiedene Argonverhältnisse ergeben, da im Elsaß derartige Vorgänge unbekannt sind. Die gleichen Meßergebnisse für beide Lager schließen jedoch diese Möglichkeit aus. Es wäre immerhin möglich, daß die geothermische Tiefenstufe in dem gesamten Gebiet der oberrheinischen Tiefebene infolge der vulkanischen Tätigkeit kleiner gewesen ist. Man kann aber nicht annehmen, daß das Gebiet der Lagerstätte, der wir unsere Proben entnommen haben, einer höheren Temperatur als 80°C ausgesetzt war. Dies dürfte wohl als Maximum angesehen werden. Der Höhepunkt des Vulkanismus der oberrheinischen Tiefebene wird jedoch noch in das Oligozän datiert. Zu einer Abschätzung erscheint es daher plausibel, eine stetige Abnahme der Temperatur anzunehmen. Setzen wir extreme Verhältnisse an und unterstellen das Lager ein Drittel der Zeit einer Temperatur von 80°C, ein Drittel 60°C und das letzte Drittel der heutigen Temperatur von etwa 40°C, so würde sich aus unseren Berechnungen ergeben, daß die experimentell gefundene Altersangabe im Maximum um 25% zu niedrig sein könnte.

Zusammenfassend ergeben unsere Messungen für das untere Oligozän ein Alter von 21 $\pm$ 3 Mill. Jahren. Selbst bei geologisch ungünstigsten Bedingungen, die wir oben diskutiert haben und die das Resultat beeinflussen könnten, kann sich der Wert höchstens um 25% erhöhen. Wir glauben daher, daß man das absolute Alter der jüngeren Tertiär-Formationen niedriger ansetzen muß als man es bisher getan hat.

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Application de la methode du RaD a la mesure de l'age "chimique" d'un minerai d'Uranium

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ABSTRACT

The RaD method suggested by F. G. Houtermans for the determination of the "chemical" age of uranium minerals consists in the measurement of Pb/U, from the ratio RaD/Pb. Since RaD is an isotope of lead, this ratio can be determined on any quantity of lead from the mineral. In this way the quantitative analyses of uranium and lead are avoided. The determination can be carried out on an extremely small quantity of matter. The conditions under which the method is applicable, and the ways of measuring RaD, are discussed.

A confirmation has been obtained with two samples of pitchblende from Shinkolobwe: the ratio Pb/U was determined on the one hand by chemical analysis, and on the other by the RaD method. All the measurements of the two methods were carried out independently at the second Physical Institute of the University of Gottingen, and at the Centre de Physique Nucléaire de l'Université Libre de Bruxelles. One method of lead determination by dithizone extraction and polarography is described in detail. The technique of measuring the RaD by counting the beta particles of RaE was perfected. The ratios Pb/U determined by the two methods agree within the experimental errors.

The advantages of the RaD method are summarized in the conclusion.

La Methode du RaD Pour la Determination du Rapport Plomb-uranium

Les travaux de Nier (1939 et 1941), de Holmes (1945–46) et d'autres, ont montré que la plus sûre des méthodes radioactives de détermination d'âge, à côté de la méthode du Rb/Sr encore à ses débuts, est la méthode au Pb contrôlée par l'analyse isotopique du Pb radiogénique.

Les points de repère de notre échelle des temps géologiques ont été établis par cette méthode en prenant comme critère la concordance des âges obtenus par les 4 rapports RaG/U, AcD/AcU, ThD/Th et AcD/RaG.

Les trois premiers rapports fournissent trois mesures indépendantes de l'âge du minéral et nécessitent la connaissance exacte des rapports chimiques Pb/U et Pb/Th.

Le rapport AcD/RaG ne nécessite pas d'analyse chimique du Pb et de l'U, mais une analyse isotopique du Pb. Ce rapport, comme Nier l'a montré, dépend très peu des pertes relatives en Pb et U.

Holmes (1945–46), Wickman (1943) et d'autres ont discuté les causes d'erreur des méthodes citées et ont corrigé quelques uns des résultats isotopiques de Nier (1939 et 1941) pour les pertes en Pb, U ou émanation grâce à la connaissance des rapports chimiques. Ils ont démontré par là que les méthodes modernes de mesure d'âge basées sur la composition isotopique du Pb ne rendent en aucune manière superflues les méthodes classiques basées sur la détermination des rapports

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chimiques U/Pb et Th/Pb et qu'il est toujours nécessaire de pouvoir mesurer ces rapports d'une manière aussi précise que possible.

La précision sur l'âge "isotopique" est souvent illusoire pour les minéraux relativement jeunes.

Comme on le voit d'après l'équation:

$$\frac{\text{AcD}}{\text{RaG}} = \frac{1}{139} \cdot \frac{e^{\lambda_{\text{AcU}} t} - 1}{e^{\lambda_{\text{UI}} t} - 1}$$

le rapport AcD/RaG pour $\lambda_{\text{AcU}} t \ll 1$ devient:

$$\frac{\text{AcD}}{\text{RaG}} = \frac{1}{139} \cdot \frac{\lambda_{\text{AcU}} t}{\lambda_{\text{UI}} t} = 4{,}6\%$$

c'est-à-dire que pour des âges qui ne sont pas supérieurs à la période de AcU ($7{,}07.10^8$ ans), t n'entre que dans le terme du second ordre. L'erreur relative sur t sera à peu proportionnelle à l'erreur sur la différence entre le rapport expérimental $\frac{\text{AcD}}{\text{RaG}}$ et 4,6% et non à l'erreur expérimentale sur AcD/RaG.

La méthode classique de mesure d'âge par le rapport chimique Pb/U

La méthode chimique classique de détermination de l'âge d'un minéral contenant de l'U et pas de Th consiste à déterminer la teneur en Pb et U par des analyses quantitatives et à calculer l'âge d'après le rapport des masses de Pb/U.

Dans ce qui suit, les symboles chimiques représentent des masses et les symboles entre parenthèses des nombres d'atomes.

En faisant les hypothèses que tout le Pb soit du Pb radiogénique, c'est-à-dire qu'il n'y ait pas de Pb "ordinaire" accessoire, et qu'il n'y ait eu aucune perte en Pb et U depuis la formation du minéral, on a la relation connue:

$$\frac{\text{Pb}}{\text{U}} = \frac{(\text{RaG})\text{A}_{\text{RaG}} + (\text{AcD})\text{A}_{\text{AcD}}}{(\text{U}_{\text{I}})\,[\text{A}_{\text{UI}} + \varepsilon \text{A}_{\text{AcU}}]} \tag{1}$$

où A_i = masse atomique de l'isotope en indice

ε = rapport actuel du nombre d'atomes $\frac{(\text{AcU})}{(\text{U}_{\text{I}})}$

Soit T_1 et T_2 les périodes de U_I et AcU; λ_1 et λ_2 leurs constantes radioactives, on a les relations:

$$(\text{RaG})/(\text{U}_{\text{I}}) = (e^{\lambda_1 t} - 1) = e^{\frac{0{,}693.t}{T_1}} - 1 \tag{2}$$

$$(\text{AcD})/(\text{U}_{\text{I}}) = \varepsilon(e^{\lambda_2 t} - 1) = \varepsilon(e^{\frac{0{,}693.t}{T_2}} - 1) \tag{3}$$

Pour les minéraux ayant un âge inférieur à 1200.10^6 ans, on peut remplacer la fonction exponentielle (2) par le premier terme de son développement en λt, et la fonction exponentielle (3) par les deux premiers termes. On fait une erreur

de 3% seulement sur 1200.10^6 ans en utilisant au lieu des relations exponentielles, la relation quadratique:

$$t_{\text{années}} = t_1 - \frac{K}{2} t_1^2 \tag{4}$$

où t_1 est l'âge "linéaire" directement proportionnel au rapport Pb/U (Keevil, 1939).

Avec les constantes données dans la tableau 1, on obtient les équations (5) qui suffisent dans la plupart des cas pratiques pour calculer l'âge en fonction du rapport Pb/U

$$\left.\begin{aligned} t_1 \text{ (âge "linéaire" en années)} &= 7{,}23.10^9 \frac{\text{Pb}}{\text{U}} \\ t_{\text{années}} &= t_1 - \frac{K}{2} t_1^2 \\ K &= 1{,}953.10^{-10}\, a^{-1} \end{aligned}\right\} \tag{5}$$

Les âges donnés au tableau 2 ont été calculés d'après les fonctions exponentielles exactes.

Tableau 1. *Valeur des constantes utilisées*

Masses atomiques physiques =

$Pb^{206} = 206{,}051$ $\quad U^{238} = 238{,}146$

$Pb^{207} = 207{,}054$ $\quad U^{235} = 235{,}13$

$$\frac{U^{238}}{U^{235}} = 139{,}0$$

$T_{U_1} = 4{,}51\ 10^9$ a $\quad T_{AcU} = 7{,}07\ 10^8$ a

$\lambda_{U_1} = 1{,}5369\ 10^{-10}\ a^{-1}$ $\quad \lambda_{AcU} = 0{,}98041\ 10^{-9}\ a^{-1}$

$$\alpha(t) = \frac{(Pb^{206})}{(Pb^{207})} = 139\ \frac{e^{\lambda_{UI} t} - 1}{e^{\lambda_{AcU} t} - 1}$$

$$\dot{N} = \frac{\text{nombre de désintégrations RaD}}{\text{sec. mg Pb radiogénique}}$$

$$= \frac{139\,\lambda_{UI},\ 6{,}0227.10^{23}}{139,\ 206{,}051(e^{\lambda_{UI} t} - 1) + 207{,}054(e^{\lambda_{AcU} t} - 1)}$$

A_{Pb} = mass atomique du Pb radiogénique

$$A_{Pb} = \frac{206{,}051 + 1/\alpha\ 207{,}054}{(1 + 1/\alpha),\ 1{,}000275}$$

La méthode radiochimique de mesure du rapport Pb/U

Une famille radioactive est dite en équilibre lorsqu'il y a autant d'atomes de chaque espèce qui apparaissent que d'atomes qui disparaissent.

Si λ_0 et n_0 sont respectivement la constante de désintégration et le nombre d'atomes de l'élément initial, et λ_i et n_i, la constante de désintégration et le nombre

Tableau 2

Age en millions d'années: t	*Masse atomique chimique du Pb radiogénique: A*	*Nb. désintégr. RaD par sec. et mg de Pb = N*	*Rapport des nb. atomes* $(Pb^{206})/(Pb^{207})$	*Rapport des masses Pb/U en%*
100	206,040	877,6	20,90	1,395
200	206,042	434,6	20,08	2,816
300	206,044	286,9	19,18	4,266
400	206,046	213,0	18,35	5,745
500	206,048	168,0	17,55	7,285
600	206,051	139,1	16,77	8,796
700	206,053	118,0	16,01	10,37
800	206,056	102,2	15,27	11,98
900	206,059	89,83	14,55	13,62
1000	206,062	79,95	13,86	15,31
1100	206,065	71,86	13,20	17,03
1200	206,068	65,12	12,55	18,79
1300	206,072	59,40	11,93	20,60
1400	206,076	54,50	11,33	22,45
1500	206,080	50,24	10,75	24,35
1600	206,084	46,51	10,20	26,31
1700	206,088	43,21	9,663	28,32
1800	206,093	40,27	9,152	30,38
1900	206,098	37,64	8,662	32,51
2000	206,103	35,25	8,193	34,71

d'atomes du $i^{ème}$ descendant, on a, en supposant que ce dernier ne se trouve pas dans un embranchement de la famille:

$$\lambda_i n_i = \lambda_0 n_0 \tag{6}$$

Cette relation est souvent utilisée, par exemple lors du dosage de l'U dans les roches, par la mesure du Ra et du Rn en équilibre.

D'après (6), pour mesurer n_0 il n'est pas nécessaire de connaitre séparément λ_i et n_i, mais il suffit de mesurer $\lambda_i n_i$, soit le nombre de désintégrations par unité de temps de l'un quelconque des membres de la famille.

La méthode déjà démontrée par l'un de nous (Houtermans, 1951) et appliquée ici consiste essentiellement à faire cette mesure sur un descendant de nombre atomique 82, c'est-à-dire un isotope du Pb. On sait que dans la famille de U_I, deux descendants ont 82 comme nombre atomique, à savoir le RaB et le RaD. Dans les familles de l'Ac et du Th, le produit B est le seul isotope du Pb. Tous ces éléments se comportent comme le Pb stable dans les réactions chimiques.

Au cours de toute séparation chimique, les rapports RaD/Pb et ThB/Pb sont invariables, compte tenu de la décroissance radioactive.

La méthode proposée ici pour la mesure de l'âge est basée sur la mesure d'un desrapports RaD/Pb; RaB/Pb; AcB/Pb et ThB/Pb.

Elle revient à mesurer l'activité spécifique du Pb contenu dans un minéral radioactif, c'est-à-dire le nombre de désintégrations radioactives par seconde et par gramme de plomb.

L'avantage est dû au fait que ces rapports sont indépendants de toute perte de Pb et qu'ils peuvent être mesurés sur une fraction quelconque du Pb total. On évite ainsi toute analyse de U et Th et l'analyse quantitative du Pb dans le minéral.

Cette méthode n'apporte rien d'essentiellement nouveau aux méthodes chimiques bien connues, mais permet des déterminations plus aisées grâce à sa simplicité et à sa sensibilité.

Dans le présent travail, nous avons eu comme but d'appliquer la méthode radiochimique à un minerai d'U sans Th. La mesure du rapport RaD/Pb permettra de calculer le rapport Pb/U et de le comparer au résultat obtenu par l'analyse chimique de Pb total et de U total.

Pour des minéraux contenant à la fois U et Th, la mesure de Pb/U par voie radiochimique comporterait la détermination non seulement du rapport RaD/Pb mais aussi de ThB/Pb. Ce problème sera traité dans un autre travail.

Méthode du RaD

La méthode du RaD consiste à mesurer Pb/U par RaD/Pb.

D'après les données du tableau 1, on a établi la relation entre l'âge d'un minéral d'U et l'activité spécifique de son Plomb (exprimée par $\dot{N}$ = nombre de désintégrations du RaD par mg de Pb et par seconde).

Cette relation a été calculée pour un certain nombre de valeurs de t; les résultats sont donnés au tableau 2, 3e colonne.

La méthode du RaD n'est valable que si l'U et le RaD sont en équilibre radioactif dans l'échantillon examiné. Cet équilibre peut être perturbé par la perte d'un des éléments intermédiaires (Io, Ra, Rn), si cette perte a eu lieu depuis un temps assez récent pour que l'équilibre avec le RaD n'ait pu encore se rétablir.

Ainsi dans le cas d'une perte d'Io pendant les derniers 5.10^5 ans, la méthode du RaD donnera des valeurs systématiquement trop élevées pour le rapport Pb/U.

Le RaD peut se mesurer par différentes méthodes: la mesure directe de son rayonnement β est difficile par suite de la faible énergie (E. max: 0,025 MeV) de ce rayonnement. Il est par contre aisé de mesurer le RaD par les β de son descendant direct le RaE (E. max: 1,17 MeV) ou par les α du RaF.

Mesure par le RaE

La mesure de l'activité β du RaE peut se faire avec un compteur dont le rendement pour le RaE a été préalablement déterminé avec un étalon.

Si l'on connaît le moment exact de la séparation du Pb et la proportion de RaE éventuellement entraîné, on peut calculer la quantité de RaE qui a recru à partir du RaD et mesurer ce dernier par une seule détermination du RaE à un moment donné.

Dans le cas contraire, on doit faire au moins deux mesures à des moments différents pour pouvoir extrapoler la quantité de RaE à l'équilibre. On peut aussi attendre un temps suffisant pour que l'équilibre RaD—RaE soit certainement établi, soit un mois environ.

Mesure par le RaF

Le RaF ou polonium se mesure par son activité α.

Les méthodes classiques utilisent la chambre d'ionisation ou le compteur proportionnel. Les méthodes les plus sensibles sont cependant basées sur les émulsions photographiques nucléaires.

La méthode de la double émulsion se prête particulièrement bien au dosage des radioéléments α sur de très petites quantités de solution (Picciotto, 1949): une goutte de l'ordre de 10^{-3} cc est déposée sur une plaque nucléaire et recouverte d'une seconde couche d'émulsion. Tous les α émis sont ainsi comptés. Cette méthode offre de plus l'avantage de pouvoir contrôler d'une facon très sensible les impuretés de Ra, on sait en effet que pour des temps d'exposition de quelques jours, une fraction calculable (Flament, 1948) des α du Ra se présente sous forme d'étoiles à 4 branches.

La période du Po (140 j.) est trop longue pour pouvoir attendre l'équilibre avec le RaD. Il faut à un moment connu éliminer le Po et attendre sa recroissance à partir du RaD pendant un temps donné. Deux possibilités sont offertes pour la mesure: (*a*) mesurer l'activité α recrue après un temps déterminé. (*b*) mesurer le nombre total d' α émis depuis le moment de la séparation du Po jusqu'à un temps t (méthode intégrale).

La mesure du RaD par le Po sera discutée en détail dans un autre travail.

Avantages et possibilitiés de la méthode du RaD

Au point de vue chimique, la méthode du RaD ne nécessite aucun dosage de U, soit direct, soit par la mesure du Ra; elle ne nécessite pas l'analyse quantitative du Pb du minéral, mais seulement la séparation d'une quantité connue de Pb représentant une fraction quelconque du Pb total.

La période du RaD étant de 22 ans, on peut appliquer la méthode du RaD à des échantillons de Pb séparés depuis de nombreuses années à condition de connaître la date de séparation à un an près. Par exemple, toutes les préparation de Pb effectuées à une date connue par Hönigschmid, Baxter, Kuhn pour la détermination de la masse atomique du Pb uranique ou pour l'analyse isotopique conviennent parfaitement.

La précision est à peu près indépendante de l'âge du minéral, car le rapport Pb/RaD est pratiquemment proportionnel à l'âge jusqu'à 5.10^8 ans (voir tableau 2).

On peut se rendre compte de la sensibilité de la méthode en observant que 1 mg de Pb d'un minerai d'U âgé de 200 millions d'années émet environ 26.000 désintégrations par minute. La mesure du RaD par l'observation photographique des α du Po pourrait se faire sur 10^{-7} à 10^{-8} g de Pb.

La sensibilité de la méthode RaD/Pb est donc uniquement limitée par la mesure de Pb. Les méthodes d'analyse de traces: colorimétrie à la dithizone, polarographie, spectroscopie, permettent de mesurer de 1 à 10 microgrammes de Pb à quelques pourcent près.

La méthode la plus sensible actuellement connue est celle de dilution isotopique réalisée par spectroscopie optique (V. Buttlar, 1952).

Au cours de cette seule analyse quantitative de Pb, le RaD présent peut être utilisé comme traceur radioactif. Si l'activité spécifique du Pb est trop faible pour être mesurée avec précision au compteur, on peut le tracer en ajoutant du ThB qui, décroissant rapidement, ne perturbera pas la mesure ultérieure du RaD.

Verification Experimentale de la Methode du RaD sur la Pechblende de Shinkolobwe

Pour vérifier la méthode du RaD, nous avons choisi la pechblende de Shinkolobwe (Congo Belge), particulièrement pauvre en Th et qui a fait déjà l'objet de nombreuses études géochronologiques (voir bibliographie dans (Cahen, 1950)).

Grâce à l'aide de Monsieur L. Cahen, Conservateur Adjoint au Musée du Congo, nous avons pu disposer de deux échantillons particulièrement purs.

Les rapports Pb/U et RaD/Pb ont été déterminés sur chacun de ces deux échantillons. A titre de contrôle, toutes les mesures ont été faites indépendamment, d'une part, au Centre de Physique Nucléaire de l'Université Libre de Bruxelles et d'autre part, au IIe Institut de Physique de l'Université de Göttingen. Les résultats seront donnés séparément pour pouvoir apprécier la reproductibilité des mesures.

Le but de ces mesures est essentiellement de comparer les valeurs de Pb/U obtenues directement par les méthodes chimiques, à celles obtenues par la méthode du RaD. La question de la position de la pechblende de Shinkolobwe dans l'échelle géochronologique absolue sera discutée dans une autre publication.

Description des echantillons

1. Sh B—numéro du Musée: RG.2233: Uraninite en cristaux cubiques de quelques mm avec cristaux d'or ou de sels d'or—Aucune trace de produits d'altération. Résidu insoluble dans l'HNO_3: 0,20% dont 0,18% d'or.

2. Sh C, numéro du Musée RG.2236: Pechblende massive d'aspect amorphe, noire, très homogène—Filonets extrêmement minces de produits jaunes d'altération. L'échantillon dissous a été prélevé dans une région exempte de toute trace de produit d'altération. Résidu insoluble dans l'HNO_3 : 0,5%.

Ces deux échantillons ont été dissous à chaud dans de l'HNO_3 à 30% pour préparer les deux solutions suivantes:

Sh BO contenant 26,8 gr de pechblende par litre.

Sh CO contenant 9,7 gr de pechblende par litre.

Les résidus insolubles, testés au compteur, ne montraient aucune trace de radioactivité, ce qui garantit que le rapport Pb/U de la solution est certainement le même que dans l'échantillon.

A. Mesure du rapport Pb/U par la methode chimique

Le calcul de l'âge par la mesure du rapport Pb/U nécessite le dosage de Pb et d'U.

Méthodes d'analyse

Dosage de l'uranium

Le dosage gravimétrique de l'U a donné des résultats satisfaisants. Nous avons utilisé la méthode classique de précipitation de l'uranate d'ammonium après séparation des autres cations du groupe de l'ammoniaque par précipitation en milieu carbonaté (voir par exemple: "Analytical chemistry of the Manhattan Project. National nuclear energy series." McGraw-Hill (1950).)

Les précautions usuelles ont été prises pour éviter la présence de CO_2 lors de la précipitation de l'U. L'absence d'U dans les filtrats a été vérifiée par l'absence de toute activité recroissant avec une période de 24,1 jours (UX_1). L'uranate d'ammonium a été calciné à 900° jusqu'à constance de poids et pesé comme U_3O_8.

Dosage du Pb

Colorimetrie à la dithizone—Les mesures colorimétriques rapportées dans les résultats de Göttingen ont été effectuées par Mmes M. Leopoldi et I. Houtermans dans les laboratoires de la firme *Siemens et Halske*. La technique suivie est décrite dans (Fischer et Leopoldi, 1933, 1940).

Dosage polarographique—On sait que le dosage gravimétrique du Pb à l'état de sulfate après séparation par H_2S est une opération délicate, spécialement si l'on opère sur de petites quantités. Nous avons pu déceler des pertes de Pb de plusieurs pourcent dans les filtrats des sulfures et des sulfates, soit par traçage radioactif du Pb par le ThB, soit par polarographie.

La gravimétrie par le sulfate est certainement possible et peut donner des résultats très précis (Hecht et Donau, 1940). Toutefois, la méthode décrite ici, basée sur la séparation du Pb par la dithizone et le dosage par polarographie nous a semblé plus maniable et surtout plus rapide.

Elle offre l'avantage important d'isoler du Pb radioactivement pur qui est ainsi prêt à être utilisé pour la mesure du RaD.

Détails techniques

Prise: 2 cc de la solution nitrique contenant environ 60 mg de pechblende. On ajoute un cc de chlorydrate d'hydrazine à 2% pour réduire le Fe^{+++}, 3 cc d'ac tartrique à 50% et 3 cc d'ac citrique à 50% pour complexer les cations susceptibles de précipiter avec l'ammoniaque.

On doit éviter l'addition de KCN qui précipite du cyanure de Pb. On ajoute de l'ammoniaque 1/1 jusqu'à pH 9,5. La solution alcaline de pechblende est extraite par une solution de 200 mg à 500 mg de dithizone par kilo de chloroforme. L'extraction est faite par fraction de 10 cc de dithizone jusqu'à persistance de la coloration verte de cette dernière.

La solution est extraite une dernière fois avec du chloroforme pur. Tout le Pb est alors dans la solution chloroformique rouge. En extrayant cette dernière par NO_3H à 1/100 jusqu'à persistance de la coloration verte de la dithizone, tout le Pb repasse en solution aqueuse.

La solution nitrique contenant le Pb est lentement évaporée à sec dans un creuset. Si les solutions doivent servir également à la mesure du RaD, il est prudent d'employer des creusets de quartz, le platine commercial étant souvent contaminé par du Ra.

Le résidu est repris et évaporé 2 fois avec de l'HNO_3 concentré pour détruire les traces de dithizone entraînées.

L'HNO_3 est éliminé en reprenant 3 fois par 5 cc d'eau et en portant à sec. Le résidu cristallin blanc de $(NO_3)_2Pb$ est prêt à être mis en solution pour l'analyse polarographique.

Polarographie—Les analyses polarographiques ont été faites suivant les directives de M. L. Gierst, assistant au laboratoire de chimie analytique de l'U.L.B.

Les solutions étant relativement concentrées en Pb (de l'ordre de 1 gr par litre), il n'a pas été nécessaire d'éliminer complètement l'oxygène. Deux milieux ont été utilisés:

1. Milieu NaOH: le $(NO_3)_2Pb$ est repris par 10 cc de NaOH 1N contenant 0,4 g/litre de gélatine et 20 g/l de SO_3Na_2 qui agit comme agent désoxygénant. Le Pb passe à l'état de plombite, soluble en présence du sulfite. Environ 70% de l'oxygène présent est éliminé par cette méthode qui a l'avantage de précipiter la presque totalité des impuretés qui pourraient être présentes. En l'absence de gélatine, l'onde du Pb présente un maximum très prononcé qui perturbe les mesures.

2. Milieu HCl: le $(NO_3)_2Pb$ est redissous dans 10 cc d'HCl 1N contenant 0,4 gr de gélatine par litre. L'addition de 10 mg de marbre avant la polarographie provoque un dégagement de CO_2 qui entraîne près de 99% de l'O_2.

Des essais effectués par les deux méthodes ont donné des résultats parfaitement concordants.

Les solutions étalons ont été préparées à partir d'une solution standard de $(NO_3)_2Pb$ dont la teneur en Pb a été déterminée par gravimétrie du SO_4Pb.

Un volume connu de la solution standard est évaporé à sec. Le résidu est repris par 10 cc de la solution normale de NaOH ou HCl qui sera utilisée pour l'échantillon.

Dans la plupart des cas, les solutions inconnues ont été comparées avec deux étalons, l'un de concentration légèrement inférieure, l'autre légèrement supérieure.

Les résultats obtenus ont toujours été reproductibles á moins de 2% près. On pourrait augmenter la précision en éliminant complètement l'oxygène et en travaillant dans des conditions thermostatiques.

Vérification de la méthode—L'efficacité de l'extraction a été vérifiée de la manière suivante: Trois solutions ont été préparées:

1. Solution Sh BO.
2. Solution standard (4,361 mg Pb/cc).
3. Mélange de 1 cc de Sh BO et de 1 cc de la solution standard.

Le Pb a été extrait suivant la procédure décrite ci-dessus et mesuré en milieu HCl normal.

La concentration calculée du mélange est de 3,12 g/Pb/1, la concentration mesurée donne 3,11 ± 0,03 gr Pb/1.

Correction due à la masse atomique—Dans les méthodes par comparaison (polarographie et colorimétrie), il faut tenir compte de la différence des masses atomiques du Pb radiogénique et du Pb ordinaire utilisé pour les solutions étalons. En prenant respectivement 206,051 et 207,21 on voit que la correction est de −0,57%.

Tableau 3

Uranium, gravimètrie U_3O_8

Concentration gr U/litre

	Bruxelles	*Göttingen*
Sh BO	20,7 ± 0,2	20,5 ± 0,2
Sh CO	14,32 ± 0,15	14,12 ± 0,15

Tableau 4

Plomb, concentration en gr Pb/litre

	Bruxelles (*polarographie*)	*Göttingen* (*colorimétrie*)
Sh BO	1,89 ± 0,04	1,85 ± 0,04
Sh CO	1,45 ± 0,03	1,46 ± 0,04

Tableau 5

Rapport Pb/U

	Bruxelles	*Göttingen*	*Moyenne*
Sh BO	(9,1 ± 0,3)%	(9,0 ± 0,3)%	(9,05 ± 0,3)%
Sh CO	(10,1 ± 0,3)%	(10,3 ± 0,3)%	(10,15 ± 0,3)%

B. Mesure du rapport Pb/U par la méthode du RaD

Le rapport RaD/Pb a été mesuré sur une solution contenant une quantité connue de Pb extrait de la pechblende. Les deux solutions préparées à cet effet à partir des échantillons ShB et ShC sont désignées respectivement ShB 7 et ShC 6.

Extraction et dosage du Pb

Pour mesurer le RaD dans ces solutions, il est essentiel que le Pb séparé soit radioactivement pur.

Le RaD a été mesuré par les β du RaE. Les éléments de la famille de l'U pouvant interférer dans cette mesure sont l'UX_1 et le Ra agissant par ses descendants.

La présence d'UX_1 est facile à détecter par sa décroissance avec une période de 24,1 j.

Le Ra peut être détecté avec une grande sensibilité (10^{-12} à 10^{-11} g/g) par la méthode photographique grâce à la formation d'étoiles d'α à 4 branches.

Une méthode très simple pour s'assurer de l'absence de Ra et éliminer son influence, consiste à se débarrasser du Rn et de ses descendants par barbotage d'azote dans la solution pendant quelques heures. Il faut prendre soin de faire passer préalablement l'azote dans une solution similaire pour éviter l'entraînement de vapeur d'eau par l'azote sec.

Préparation du Pb radioactivement pur

Deux méthodes ont été utilisées pour la préparation du Pb radioactivement pur.

1. *Purification par précipitation*—Le cycle suivant a été utilisé pour la préparation des solution ShB 7 et ShC 6. Départ de 10 cc des solutions nitriques de pechblende ShBO et ShCO. Evaporer à sec deux fois pour éliminer l'HNO_3. Porter à 25 cc, ajouter quelques milligrammes de $BaCl_2$ et rendre la solution lN en H_2SO_4. Centrifuger. Laver avec de l'H_2SO_4 N/2. Le précipité de SO_4Ba (+Ra) et de SO_4Pb est traité à chaud 30 minutes par une solution contenant 500 g/l d'acétate d'ammonium et 40 g/l d'acide acétique. Centrifuger.

La solution contient la majorité du Pb à l'état de complexe acétique, une partie reste fixée dans le précipité de SO_4Ba. On effectue une seconde précipitation de sulfate de Ba qui entraîne le reste du Ra.

La solution acétique est amenée à pH environ 6 par addition d'NH_4OH.

On précipite PbS à l'ébullition par une solution saturée de Na_2S, filtrer sur verre fritté, laver avec de l'HCl 0,3N et dissoudre sur le filtre par de l'HNO_3 chaud à 30% jusqu'à ce qu'il ne reste plus qu'un résidu blanc ou gris de soufre. Si le filtrat est trouble, il suffit de chauffer quelques minutes pour l'éclaircir.

Le nitrate de Pb est évaporé jusqu'à cristallisation. La solution surnageante est décantée et les cristaux lavés avec une solution d'HNO_3 à 60%. Les cristaux sont redissous dans de l'HNO_3 à 30% et cette opération est répétée 3 à 4 fois.

On obtient ainsi du $(NO_3)_2Pb$ exempt de Ra débarrassé de la majorité du Po et du RaE (Curie 1925).

Le $(NO_3)_2Pb$ est mis en solution dans de l'acide nitrique à 30%. Il est indispensable de garder ces solutions très acides pour permettre la mesure du RaE dans les compteurs à liquides. On peut éventuellement ajouter du Bi inactif pour stabiliser le RaE.

2. *Purification par la dithizone*—La dithizone permet une séparation aisée et complète du RaD parfaitement pur (Bouissieres et Ferradini, 1950). Nous avons contrôlé par la plaque photographique l'absence de Ra ($<10^{-13}$ g/g).

Toutes ces opérations peuvent être effectuées rapidement, quitte à perdre un peu de Pb. On doit se souvenir que leur but est d'isoler une certaine quantité de Pb radioactivement pur et non de séparer quantitativement le Pb.

Dosage du Pb—La concentration du Pb dans les solutions ShB7 et ShC6 a été mesurée par polarographie à Bruxelles et par colorimétrie à la dithizone à Göttingen.

Les résultats sont représentés dans le tableau 6:

Tableau 6

Plomb: concentration en g/litre

	Bruxelles	*Göttingen*
ShB7	0,45 ± 0,01	0,42 ± 0,01
ShC6	0,615 ± 0,012	—

Mesure du RaD

Méthode de mesure—Comme on l'a déjà dit, le RaD est difficile à mesurer directement par son rayonnement β de trés faible énergie.

Dans le présent travail, la concentration en RaD a été mesurée par l'activité β du RaE. En général les mesures ont été faites à l'équilibre RaD–RaE, soit 4 à 5 semaines après la séparation du Pb.

Les mesures d'activité ont été effectuées sur des solutions à teneur en Pb connue, dans des compteurs de Geiger pour liquides d'une capacité de 10 cm³. Les mesures en solution se sont montrées parfaitement stables et reproductibles à condition de se tenir en milieu très acide (5 à 10% de NO_3H) pour éviter l'hydrolyse de Pb et Bi. Pour toute sécurité, on peut ajouter du Bi inactif pour stabiliser le RaE.

Dans ce type de compteur, les corrections géométriques ainsi que celles qui sont dues à l'absorption dans l'échantillon ou dans les parois du compteur sont constantes *pour une solution de densité donnée.* Ces corrections sont comprises dans le rendement du compteur, c'est-à-dire le rapport du nombre d'impulsions du compteur au nombre de désintégrations dans un volume donné de solution. En introduisant une solution de Ra (D + E + F) dans le compteur, seuls les β du RaE sont comptés. Pour mesurer quantitativement le RaE, il est nécessaire de déterminer le rendement du compteur à l'aide d'une solution étalon.

Preparation d'une solution etalon de Ra (D + E)—La description détaillée de la préparation d'un étalon de RaD sera publiée séparément. A un temps $t = 0$, une quantité connue de Rn a été introduite dans un tube de verre mince. Le Rn a été dosé en comparant son activité γ à celle d'une source étalon de Ra.

Au temps t_1 le tube de verre a été brisé et le RaD formé, extrait par ébullition dans de l'acide nitrique contenant du Pb et du Bi inactif comme support. Il est facile de calculer la concentration en RaD de cette solution, l'erreur sur la concentration en RaD dépend de la précision sur l'étalon de Ra utilisé. L'activité (nombre de désintégrations du RaD par sec. et cm³) de cette solution a été calculée en prenant la période du RaD égale à 22 ans.

A titre de confirmation, un échantillon solide de Ra (D + E) a été préparé en évaporant une goutte de poids connu de la solution étalon sur un support en mica mince. Son activité a été comparée à celle d'un étalon similaire prêté par l'Institut du Radium de Paris mais connu à 10% près seulement. Les mesures se sont montrées concordantes.

Resultats des mesures de RaD

La teneur en RaD de chaque solution a été mesurée avec 4 compteurs différents à Bruxelles et à Göttingen. Le rendement des compteurs pour Ra(D + E) était de l'ordre de 2%.

Les résultats sont présentés dans le tableau 7. L'erreur relative de 3% comprend une erreur de 2% sur l'activité de la solution étalon et une erreur de 2% sur la reproductibilité des mesures au compteur.

Tableau 7. Activités des solutions de Pb en nombre de désintégrations du RaD par sec. et par cc de solution

	Bruxelles			*Göttingen*		
N° compteurs	*L 1*	*H 2*	*Moyenne*	*D2*	*MA3*	*Moyenne*
ShB7	58,7 ± 1,7	59,5 ± 1,8	59,1 ± 1,8	56,8 ± 1,7	59,0 ± 1,8	57,9 ± 1,7
ShC6	75,3 ± 2,2	74,6 ± 2,2	74,9 ± 2,2	74,6 ± 2,2	76,0 ± 2,2	75,3 ± 2,2

Le tableau 8 donne le nombre de désintégrations du RaD par mg de Pb en prenant pour les activités les moyennes du tableau 7 et pour les concentrations

en Pb les valeurs du tableau 6. Les rapports Pb/U ont été calculés d'après ces activités spécifiques. A titre de comparaison, les rapports Pb/U mesurés directement par la méthode chimique sont repris du tableau 5 et donnés à la dernière ligne.

Tableau 8. Activités spécifiques du Pb de ShB et ShC et comparaison des rapports Pb/U obtenus par les deux méthodes

	Bruxelles	*Göttingen*	*Moyenne*
ShB			
Nb. dés RaD / sec. mg Pb	131,6	138,2	134,9 ± 4,7
Pb/U Méthode RaD	9,35%	8,90%	(9,12 ± 0,32)%
Pb/U Méthode chim.	9,09%	9,00%	(9,045 ± 0,32)%
ShC			
Nb. dés RaD / sec. mg Pb	121,7	122,5	122,1 ± 4,3
Pb/U Méthode RaD	10,10%	10,04%	(10,07 ± 0,35%)
Pb/U Méthode chim.	10,06%	10,32%	(10,19 ± 0,35)%

On voit que les discordances portent surtout sur les analyses de Pb. Le tableau 7 montre que les mesures d'activité concordent à moins de 1% près.

3. Age "Chimique" de la Pechblende de Shinkolobwe

Age chimique

L'âge de la pechblende de Shinkolobwe ne pourra être discuté que lorsque l'on connaîtra la composition isotopique du Pb. Les analyses isotopiques et les déterminations des rapports Pb/U étendues à d'autres échantillons feront l'objet d'une prochaine publication ou seront comparés les âges obtenus par les 3 méthodes au Pb et où sera discuté la position de la pechblende de Shinkolobwe dans l'échelle géochronologique.

Dans ce but, le Pb des échantillons ShB et ShC a été envoyé dans deux laboratoires (IIe Institut de Physique à Göttingen, Dr. H. Ehrenberg et Prof. W. Paul et Laboratoire de Géophysique à Toronto, Dr. C. B. Collins et Prof. T. Wilson) qui ont bien voulu prêter leur collaboration pour établir le spectre de masse. Les résultats préliminaires confirment ceux de Nier et permettent de conclure avec certitude à l'absence de Pb ordinaire.

D'autre part, on sait que la teneur en Th de la pechblende de Shinkolobwe est pratiquemment négligeable.

La très faible teneur en Th a été également prouvée par la méthode radioactive suivante qu sera publiée en détail plus tard:

Du Pb a été extrait d'une solution de pechblende et son activité a été suivie pendant plusieurs jours. Lorsque le Th est présent, on extrait en même temps que le Pb, le ThB dont la période est environ de 10 heures. Ce ThB est en équilibre avec le ThC (isotope du Bi) en quelques heures. L'évolution de l'activité pendant les 24 premières heures est alors uniquement fonction de la décroissance du Th (B + C), alors que l'activité du RaE recroissant avec une période de 5 jours est encore négligeable.

Cette méthode permet de mesurer rapidement le rapport Th/U d'un mineral radioactif même lorsque ce rapport est très grand ou très petit. On doit à cet effet disposer d'un compteur dont le rendement soit connu pour le Ra (D + E) et pour le Th (B + C), nos compteurs ont montré un rendement de 10 à 12% pour les solutions de Th(B + C).

Par cette méthode, on a trouvé pour la pechblende de Shinkolobwe Th/U $< 0{,}5\%$ (Buttlar, 1952).

Dans de pareilles conditions (absence de Th et de Pb ordinaire) et si le minerai n'a subi aucune perte en Pb ou en U au cours de son histoire géologique, le rapport Pb/U permet une bonne détermination de l'âge.

D'après de nombreuses observations, les pertes en U ou Pb sont généralement faibles dans les uraninites noires et bien cristallisées, ce qui est le cas de notre échantillon ShB. L'échantillon ShC, quoique d'aspect amorphe ne présente aucune trace d'altération.

On peut donc s'attendre à ce que le rapport Pb/U mesuré ici par deux méthodes indépendantes, permette déjà une bonne estimation de l'âge.

Nous entendons par âges "chimiques," les âges calculés d'après le rapport Pb/U, ils sont donnés dans le tableau 9. Les âges réels ne seront calculables qu'après obtention des rapports isotopiques. *Notons que les âges chimiques donnés au tableau 2 ont été calculés en supposant que les âges par les rapports AcD/AcU et RaG/U_I sont concordants.*

Le tableau 9 donne pour les deux échantillons étudiés, les âges chimiques basés sur les rapports Pb/U déterminés, d'une part par l'analyse chimique, d'autre part, par la méthode du RaD.

Tableau 9. *Ages "chimiques" en millions d'années*

		Bruxelles	*Göttingen*	*Moyenne*
Age par Pb/U	ShB	614 ± 20	609 ± 20	612 ± 20
	ShC	676 ± 25	691 ± 25	681 ± 25
Age par RaD/Pb	ShB	631 ± 20	603 ± 20	617 ± 20
	ShC	680 ± 25	679 ± 25	680 ± 25

Tableau 10. *Ages chimiques d'après la moyenne générale des rapports Pb/U*

(en donnant le même poids aux résultats des deux méthodes)

ShB: $614{,}5.10^6$ ans ± 18
ShC: $680{,}5.10^6$ ans ± 20

La concordance des rapports Pb/U obtenus par la méthode classique et par la méthode du RaD démontre que les conditions d'application de cette dernière sont remplies, à savoir que *dans les deux échantillons, l'équilibre radioactif était réalisé entre l'U et tous ses descendants jusqu'au RaD inclus.*

Conclusions générales

En conclusion, il nous semble utile d'insister sur les avantages de la méthode du RaD comparée à la méthode classique de détermination du rapport Pb/U:

1. Le dosage d'U n'est plus nécessaire.
2. Le dosage du Pb total est évité. Il suffit d'extraire une fraction quelconque du Pb.
3. La méthode du RaD est extrêmement rapide comparativement à la méthode chimique, elle permet d'effectuer en série un grand nombre d'analyses sur des minerais différents ou sur plusieurs échantillons du même minerai.
4. La méthode du RaD permet de mesurer Pb/U sur une masse très réduite d'échantillon.

Les mesures du RaD au compteur peuvent se faire sur 0,5 mg de Pb, soit 5 mg de notre pechblende. La mesure du RaD par les α du Po dans l'émulsion photographique pourrait se faire sur des prises de Pb de l'ordre de 10^{-7} à 10^{-8} g. La sensibilité de la méthode du RaD est alors uniquement limitée par la détermination du Pb. Les méthodes les plus sensibles permettent de mesurer 1 à 10 microgrammes de Pb. Cette possibilité de déterminer les âges chimiques sur quelques microgrammes de plomb serait du plus haut intérêt pour la détermination de l'âge chimique des inclusions radioactives des roches ordinaires (Keevil, 1939).

Remerciements—Nous sommes heureux de pouvoir remercier ici les nombreuses personnes qui nous ont aidé dans l'accomplissement de ce travail.

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Résumé

La méthode du RaD proposée par F. G. Houtermans pour la mesure de l'âge "chimique" d'un minerai d'U consiste à mesurer Pb/U par le rapport RaD/Pb. Le RaD étant un isotope du Pb, ce dernier rapport peut être déterminé sur une quantité quelconque du Pb du minéral. On évite ainsi l'analyse quantitative de U et Pb. La détermination peut se faire sur une quantité extrêmement faible de matière. Les conditions de validité de la méthode ainsi que les méthodes de mesure du RaD sont envisagées.

Une vérification a été effectuée sur deux échantillons de la pechblende de Shinkolobwe: le rapport Pb/U a été déterminé d'une part par analyse chimique, d'autre part par la méthode du RaD. Toutes les mesures par les deux méthodes ont été effectuées indépendamment à l'Institut de Physique II de l'Université de Göttingen et au Centre de Physique Nucléaire de l'Université de Bruxelles. Une méthode de dosage du Pb par extraction à la dithizone et par polarographie est décrite en détail. La technique de mesure du RaD par détection au compteur des β du RaE est largement développée. Les rapports Pb/U déterminés par les deux méthodes concordent aux erreurs expérimentales près.

Les avantages de la méthode du RaD sont résumés dans la conclusion.

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The composition of the stone meteorites and the origin of the meteorites*

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ABSTRACT

A study has been made of some 350 chemical analyses of stone meteorites available in the literature, and criteria have been applied in an attempt to select those which are more reliable. It is found that the chondrites fall into two distinct groups with regard to both the total iron content and the oxidation state of the iron. These groups cannot be related by any simple mixing process and thus indicate that the meteorites have been derived from two rather different parent objects rather than from a single body. It appears that preferential volatilization of silicates and retention of nickel-iron operating to a different extent during a high temperature stage in the evolution of the asteroids may explain the different compositions of the two groups of chondrites. The implications of these data with respect to the cosmic abundances of the elements are discussed, and it is concluded that Goldschmidt's abundances for iron and nickel are too high. It is postulated that the parent asteroids went through a low temperature accumulation process, a high temperature stage of partial melting and evaporation, a stage of collisions with smaller objects which produced brecciated and tuffitic agglomerations of material and chondrules; and finally a collision of two such objects compacted the material into the meteorites, preserving however the essential differences in composition between the two groups.

1. Introduction

Analyses of meteorites date from over a century ago up to the present time and are scattered through a wide literature, often in little known journals. A compilation of analyses of meteorites was made by Farrington, who devised at the same time a system of classification based upon their chemical composition. Merrill in 1916 also undertook to compile what he considered to be the best analyses at that time. Brown and Patterson made a compilation of 107 meteorites, mostly those of Merrill together with some new analyses added during this century. Approximately 350 stone meteorites have been analyzed and it has been the purpose of this research to study these original analyses and to select those that appear to be reliable. The analyses have been evaluated on the basis of what appears to be rather objective criteria, and attempts have been made to observe regularities. The stone meteorites show a great variety of composition, but some recent evidence indicates that their compositions are more regular than had previously been supposed, particularly among the chondrites.

2. The Classification of Meteorites

Meteorites are generally divided into irons, stony irons, and stones, according to the relative proportions of metal phase and silicate phase. The metal phase content of the stones ranges up to about 35%, and from this point the stony irons form a fairly transitional group leading into the irons. The stones are further subdivided into chondrites, characterized by the presence in large or small numbers of rounded grains or aggregates of silicate material embedded in the silicate

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matrix, and achondrites which do not possess these chondrules and have a crystalline structure generally similar to that found in the terrestrial igneous rocks. In his catalogue of 1940, COULSON lists 1258 known meteorites broken down as follows: 19 unclassified, 456 irons, 58 stony irons, and 725 stones further divided into 56 achondrites, 566 chondrites, and 103 unclassified [13].

The relative abundance of the stones must be even greater than the above figures imply, since the irons are more easily recognized as meteorites when found. Thus the average composition of all meteorites should be based on those seen to fall, and WATSON, using these as a basis, gives the proportions in weight per cent as irons 5, stony irons 1·5, and stones 93·5 [26].

The classification most widely known and used in the subdivision of the above groups was introduced by ROSE in 1862 and later modified by TSCHERMAK and BREZINA. It is based purely on physical characteristics. We give here a modified form of this system as it is applied to the stone meteorites, since reference will be made to various groups of this classification throughout this paper. To the symbols for the groups we list, the letters a and b are appended to form sub-groups representing respectively "veined" and "brecciated" members of the groups.

Rose-Tschermak-Brezina Classification of Stony Meteorites

A. *Chondrites—C.*

1. White Chondrites—*Cw.* White rather friable mass with white chondrules, chondrules generally few in number.

2. Intermediate Chondrites—*Ci.* Firm, polishable mass with white and grey chondrules which break with the matrix. Transitional from 1–3.

3. Grey chondrites—*Cg.* Firm grey mass with various types of chondrules which break with the matrix.

4. Spherical Chondrites—*Cc.* Friable mass with firm chondrules of radiate structure not breaking with the mass.

5. Crystalline Spherical Chondrites—*Cck.* Transitional between 4 and 6.

6. Crystalline Chondrites—*Ck.* Hard, crystalline mass with firm chondrules of radiate structure, breaking with the mass.

7. Black Chondrites—*Cs.* Dark or black mass, chondrules of various types breaking with the matrix. Generally thought to be ordinary types with dark colour caused by heating.

8. Carbonaceous Chondrites—*K.* Dull black, friable chondrites with free carbon, low specific gravity, highly oxidized, nickel-iron nearly or wholly wanting.

9. Enstatite Chondrites—*Cek.* Chondrites composed of enstatite and nickel-iron in a hard crystalline mass, with firm chondrules of radiate structure, breaking with matrix.

10. Amphoteric Chondrites—"*CAm.*" We have introduced this symbol to designate the class proposed by WAHL and WIIK to include Jelica and Vavilovka, formerly classed as amphoterites (see below). Brecciated and tuffitic structure, chondrules scarce. We have also added Manbhoom to this group.

B. *Achondrites*

I. Calcium poor, magnesium rich stones. Poor in nickel-iron.

1. Bustites—*Bu.* Chiefly enstatite.

2. Chladnites—*Chl.* Chiefly hypersthene.

3. Chassignites—*Cha.* Chiefly olivine.

4. Amphoterites—*Am.* Hypersthene with olivine. Structure sometimes chondritic (see "*CAm*" above). Rodites (*Ro*) are brecciated amphoterites.

5. Ureilites—*U.* Clinobronzite and olivine.

II. Calcium-aluminum rich, magnesium poor stones, poor in nickel-iron.

1. Angrites—*A.* Chiefly augite or diopside.

2. Eucrites—*Eu.* Clino-hypersthene with anorthite.

3. Howardites—*Ho.* Hypersthene, clino-hypersthene, and anorthite. Generally brecciated.

4. Sherghottites –*She.* Clino-hypersthene with maskelynite (glassy plagioclase).

Prior [17] introduced a new classification based on the proportions of iron to nickel in the nickel iron and MgO to FeO in the silicates. As later modified by him [18] this classification is roughly the same as that listed above for the achondrites, but divides the chondrites into three groups: enstatite chondrites, bronzite-olivine chondrites, and hypersthene-olivine chondrites. This system has the advantage of being based on chemical composition but so far has not come into general use. Reference to Prior's system will be made in more detail later on.

3. Selection of Analyses and Construction of Tables

Some 350 analyses of stone meteorites are to be found in the literature dating back to the beginning of the nineteenth century. Two points become immediately apparent during the study of these data. First, it is clear that some analyses are of such poor quality that they should be eliminated in any study of regularities in chemical composition. For example it is possible to find several analyses of the same meteorite which differ to a great extent, and thus unless such extreme variations in a single stone exist as to make a statement of its average composition meaningless, some of the analyses must be incorrect. Moreover, analyses may be found which deviate widely from the mineralogical composition as deduced from microscopic study. Secondly, it is found that the various compilations of analyses possess errors of interpretation such that in some cases the statement of chemical composition bears little relation to the original analysis as given, and it is also clear that little effort has been made to discriminate between good and bad analyses.

Of the various compilations of meteorite analyses that we have used as a guide to the original literature [1–12], those of Farrington [5], Merrill [9], and Brown and Patterson [1] have been made with an attempt to more or less order the available data and gain information about the composition and relationships of the stones. In each of these we have found errors of interpretation due mainly to the fact that many of the original analysts gave their results in terms of various portions of the meteorite expressed to 100%. Thus it is not uncommon to find the soluble silicates, the insoluble silicates, and the metal phase each given as a separate analysis totalling 100%, and these must be put back together in the right proportions. Many of these analytical statements are more complicated and a careful reading of the text is necessary to determine exactly what has been done. In Farrington's collection the recalculations made by Wadsworth are generally

quite wrong and must be redone. In the compilations of Brown and Patterson the meteorites of Knyahinya, Lissa, Sazovice, Tabor, and Zebrak are listed as having no metal or sulphide phase, though the analyses of these phases are given in the same reference which gives the silicate phases.

A more important error, which may be termed "systematic" is due to a misinterpretation of the analytical statement of iron sulphide. Sulphur is usually stated as such, but the iron accompanying it to make FeS may be included in the FeO, included in the metallic Fe, or be given directly. In most cases it is given either in the FeO, in which case the total analysis contains too much oxygen, or in the metallic Fe. In Farrington's compilation it was apparently assumed that when not given directly this iron was always in the FeO, and thus his mineral norms which purport to show the whereabouts of this iron are quite often wrong, and averaging his analyses will result in too little iron in the silicate phase and too much in the metal phase. Merrill attempted to retabulate this iron with the metallic Fe, but erred in some cases and left it in the FeO. In the compilation of Brown and Patterson, it was apparently assumed that when not given directly the Fe for S was always in the metallic Fe, and thus in many cases their silicate phases contain too much iron. Thus in recalculating the silicate phase to 100% as they have done, the iron will be higher and the oxides somewhat lower than the correct values. In almost all cases of doubt, it is possible to establish the true location of the iron for FeS in these original analyses by noting the mineral norms as given by the author or by a careful reading of the text.

In view of the above we have attempted in each case to take the chemical analysis from the original source and in most cases this has been possible. In a few cases the original source was not available, and unless a completely reliable abstract giving the necessary information concerning FeS was available we have simply discarded the analysis. We are then faced with the problem of attempting to select the more trustworthy analyses and discard the bad. We have first of all made separate tabulations of chondrites and achondrites, since one purpose of the work was to study the relationships of and in these two groups. No selection of data was made in the case of the achondrites since the variations in composition are so great and the analyses so few that it is impossible to apply any general criteria. In the case of the chondrites however, there are some 300 analyses which indicate an exceedingly uniform composition for the group as a whole, and it is within this group that we have been able to apply certain criteria of reliability.

A chemical analysis is generally termed "bad" if it expresses incorrectly the composition of the substance analyzed. However, in the sense of the problem we wish to study the analysis may be correct but the substance itself may have been altered so that it does not possess its original composition. Thus if we wish to study the composition of the meteorites with respect to genesis, we must eliminate those whose composition has been altered by the effects of terrestrial weathering. It is well known that the principal manifestations of weathering of meteorites are water, Fe_2O_3, and NiO. Wahl [16, p. 420] has stated that water and Fe_2O_3 in considerable amounts indicate much alteration by weathering, and that the occurrence of NiO with these compounds indicates far-reaching decomposition of the nickel-iron in the stone. We have therefore first eliminated

those chondrites which show by the presence of extreme amounts of these compounds that decomposition by weathering has probably taken place. Fe_2O_3 is reported in some analyses of "finds" and may therefore be actually present in some cases, and we have not discarded analyses in which up to 3 or 4% of Fe_2O_3 are reported. In these cases we have recalculated Fe_2O_3 as FeO.

In eliminating analyses on the grounds of having been made incorrectly we have been guided mainly by the work of Wahl and Wiik [14], [15], who have performed the valuable service of checking many old analyses in which certain constituents seem to deviate markedly from the average for chondritic material. They find that all the extreme deviations which they have checked are incorrect, and thus their work substantiates the indications that the composition of the chondrites is remarkably uniform. We have eliminated those analyses which they have shown to be incorrect, and from their work and the known mineralogical requirements such as the principal occurrence of Na, K, Al, and Ca in well defined proportions in feldspars, we have adopted the following standards for eliminating analyses from our lists. Analyses are discarded when the alkalis have not been determined or found, when K_2O is greater than Na_2O, when $Na_2O + K_2O$ is greater than 3%, when CaO or Al_2O_3 is lacking, or present in extremely small amounts, when CaO is greater than about 4% or Al_2O_3 is greater than about 5%, when S is lacking or very low, or very high except in the analyses of the enstatite chondrites which are generally characterized by a high sulphur content, and when Cr_2O_3 or MnO is much greater than about 1%. We have undoubtedly included some incorrect analyses since we have at all times tried to err on the side of keeping too many rather than exclude any analyses that might be correct. When, for example, a given constituent is low or high but not to an extent of being clearly impossible the analysis is kept unless one or more other constituents are in a questionable range. Thus our table of discarded analyses shows that most have been discarded on the grounds of several constituents, indicating that the entire analysis has been poorly done. We have not used the abundance of iron in selecting analyses, since we wish to study this abundance and in fact have classified the chondrites on this basis (see below).

We have deviated from the work of Wahl and Wiik with respect to Kokta's micro-analyses of Knyahinya, Lissa, Sazovice, Tabor, and Zebrak. Wahl and Wiik have listed values of CaO, K_2O, and MnO from Kokta's analyses and redetermined these for Knyahinya. However, they have given Kokta's values for Knyahinya in per cent of the silicate phase, and thus too high, so the discrepancies are not so great as they appear. Moreover Wiik's value for CaO cannot be determined as it is given twice with different figures [14, p. 31 and 32]. We have not felt justified in discarding five analyses in view of small discrepancies in one.

As mentioned previously NiO is a common product of weathering, but it may also be present in an analysis due to incomplete separation of nickel-iron from the silicate phase. CoO is also given as a constituent of the silicate phase in some analyses, though it never appears unless NiO does also. In their compilation of analyses [1], Brown and Patterson have tabulated NiO and CoO as silicate phase constituents, and have based their arguments concerning the origin of

meteorites to a great extent on the average percent of NiO present [3]. However, if one looks at their histogram of the frequency distribution of NiO [1], one sees that, unlike the distribution curves for all other oxides, the NiO curve is a maximum at about 0%, and since negative deviations are not possible, this indicates that the true value is zero and that NiO is due either to weathering or incomplete separation of metal from silicate. PRIOR [17] mentions his doubt concerning the validity of several analyses because of NiO, and stated that the ferromagnesium minerals of chondrites contain practically no NiO, indicating incomplete separation of metal. FARRINGTON [19, p. 187] noted the marked absence of nickel from analyses of meteoritic olivine as contrasted with terrestrial olivine. WAHL [16] stated that this nickel with a proportional amount of iron should be calculated back to the metal phase, a procedure which C. RAMMELSBERG followed in the statement of his analyses. We have followed this procedure in tabulating our analyses. However, this procedure involves the assumption that not only in the case of incomplete separation but also in the case of NiO produced by weathering the ratio of iron to nickel in the metal found in the silicate phase will be the same as the ratio in the metallic nickel-iron. This may not always be true, and since large amounts of NiO would call for the transfer of very large amounts of iron back to the metal phase, we have arbitrarily eliminated those analyses in which NiO is greater than about 0·25%. We have thus discarded 18 meteorites for no other reason than the NiO content, though it is probable that in some of these Fe_2O_3 has been present in large amounts from weathering and the analyst has simply given all oxidized iron as FeO as in the case of the meteorite Jerome (see Table 1 for reference).

4. Terminology and Compilation of Analyses

In the matter of terminology we have followed the usage of COULSON's excellent catalogue [13], listing the meteorites by the names he adopts in all cases but the following in which his catalogue is in error*:

Correct Name	*Coulson's Name*
Cuero	Cuerco
Orgueil	Orguell
Sauguis	Sauguls
Schonenberg	Schoneberg
Varpaisjarvi	Varpaisjairi

Moreover, for ease of tabulation we have arbitrarily shortened Saint Christophe-la-Chartreuse to Saint Christophe. With respect to classification we have classed Jelica and Vavilovka as chondrites following WAHL, and also Manbhoom, all three being given as achondrites by COULSON. Following MERRILL [8] we have listed Novo-Urei as a chondrite, though it probably should be included with the other ureilites in the achondrites.

* Dr. WAHL kindly informs us (personal communication) that several type classifications in COULSON's cataolgue are incorrect. The Rose-Tschermak-Brezina classifications of meteorites No. 2, 4, 8, 53, 56, 62, 77 and 82 in Tables 2 and 4 have been changed in proof to those given us by Dr. Wahl, and Table 8 and the text have been modified accordingly.

Table 1. *Discarded analyses of chondrites*

No.	*Name*	*Reasons Discarded*	*Reference*
1	Achiras	Na_2O = Tr., $K_2O > Na_2O$	A. CHAUDET; Bol. Acad. Nac. Cienc. Cordoba 1951 **39** 261
2	Aguada	Na_2O = Tr., $K_2O > Na_2O$, $Al_2O_3 = 5{\cdot}56$	A. CHAUDET; Bol. Acad. Nac. Cienc. Cordoba 1951 **39** 261
3	Aguila Blanca	NiO = 1·90	E. DUCLOUX; Notas Museo La Plata 4, Geol. No. 9 1939 353
4	Albareto	Recent analysis	P. MAISSEN; Gazzetta Chim. Italiana 1880 **10** 20
5	Alessandria	MgO = 11·18, $Al_2O_3 = 8{\cdot}65$, $Na_2O = 0$	MISSAGHI; cited in [10] p. 255
6	Alfianello	MgO = 10·62, CaO = 5·05, $Cr_2O_3 = 3{\cdot}32$, $Na_2O = 0$	W. FLIGHT; Proc. R. Soc. London 1883 **35** 258
7	Alfianello	$Al_2O_3 = 0{\cdot}93$	H. VON FOULLON; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1883 **88** 433
8	Alfianello	No alkalis, Fe includes Ni	C. FRIEDHEIM; Sitz-ber. Akad. Wissen. Berlin 1888 **1** 345
9	Alfianello	CaO = 0·89	P. MAISSEN; Gazzetta Chim. Italiana 1883 **13** 369
10	Anthony	NiO = 0·91, CoO = 0·03, $SO_3 = 2{\cdot}09$, Fe includes Ni	G. MERRILL; Proc. Nat. Acad. Sci 1924 **10** 306 (Whitfield)
11	Artracoona	$Fe_2O_3 = 7{\cdot}64$, $CO_2 = 0{\cdot}42$, $H_2O = 2{\cdot}30$	A. KLEEMAN; Trans. Roy. Soc. S. Australia 1936 **60** 73
12	Athens	All Fe as Fe_2O_3, $Al_2O_3 = 14{\cdot}41$, MgO = 8·51, S = 0	S. PERRY and C. WYLIE; Pop. Astron. 1935 **43** 331 (KOUNTZ)
13	Ausson	NiO + MnO = 0·41, $Cr_2O_3 = 1{\cdot}16$	G. CHANCEL and A. MOITESSIER; Comptes Rendus 1859 **48** 269 and 479
14	Ausson	CaO = 0·80, $Na_2O = 0{\cdot}57$, $Cr_2O_3 = 1{\cdot}24$	A. DAMOUR; Comptes Rendus 1859 **49** 31
15	Ausson	CaO = 0·54, MgO = 10·68	FILHOL and LEYMERIE; Comptes Rendus 1859 **48** 198 and 348
16	Ausson	CaO = 0	E. HARRIS; cited in [4]
17	Bachmut	Fe for S uncertain	KENNGOTT; cited by O. BUCHNER, Ann. Phys. 1869 **136** 437 (WOHLER)
18	Bachmut	CaO = 0·04, Fe for S uncertain	A. KUHLBERG; cited by O. BUCHNER, Ann. Phys. 1869 **136** 437
19	Barratta No. 1	$K_2O = 1{\cdot}02 = > Na_2O$, $Fe_2O_3 = 3{\cdot}93$	A. LIVERSIDGE; J. Roy. Soc. N.S.W. 1882 **16** 31
20	Barratta No. 2	$Fe_2O_3 = 9{\cdot}48$, Ni in silicate phase = 0·48	A. LIVERSIDGE; J. Roy. Soc. N.S.W. 1902 **36** 341
21	Bettrechies	$Al_2O_3 = 0{\cdot}18$	LECOMPTE; Mem. R. Mus. Hist. Nat. Belgique No. 66 1935 (RONCHESUE)
22	Blansko	NiO = 0·21, S = 0·06	J. BERZELIUS; Ann. Phys. 1834 **33** 8; F. VON REICHENBACH, *ibid* 1865 **124** 230
23	Blithfield	NiO = 0·26, CaO = 0·87, $SO_3 = 0{\cdot}12$, $H_2O = 1{\cdot}30$	JOHNSTON and CONNOR; Trans. R. Soc. Canada 1922 **16** (Sect. 4) 187
24	Bluff	NiO = 1·59, CoO = 0·16, No alkalis	G. MERRILL; Amer. J. Sci. 1888 **36** 119 (WHITFIELD)
25	Borkut	$Na_2O = 1{\cdot}91$, $K_2O = 0{\cdot}62$, S = 0·88	J. NURISANY; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1856 **20** 398
26	Bremervorde	CaO and S not determined	F. WOHLER; J. LIEBIG'S Ann. der Chemie 1856 **99** 244
27	Bur	No alkalis, Fe for S uncertain	C. LIPPI-BONCAMBI; Universo Inst. Geog. Mil. Italy 1949 **29** 65
28	Buschof	CaO = 0·71, $K_2O > Na_2O$, Fe for S uncertain	GREWINGK and SCHMIDT; cited in [5]
29	Cabeza de Mayo	$Al_2O_3 = 0{\cdot}51$, CaO = 0·09, FeS = 20·52	S. MEUNIER; Comptes Rendus 1868 **66** 642
30	Carcote	$Cr_2O_3 = 0{\cdot}97$, Total = 97·3%	F. SANDBERGER; Neues Jahrb. Min. 1889 **2** 177 (WILL)
31	Carraweena	$Al_2O_3 = 5{\cdot}99$, $Na_2O = 1{\cdot}88$	A. ALDERMAN; Rec. S. Australian Mus. 1936 **5** 537
32	Castalia	CaO = 0, S = 0·46	J. L. SMITH; Amer. J. Sci. 1875 **10** 147
33	Cavour	$Fe_2O_3 = 11{\cdot}81$, NiO = 0·55, $K_2O > Na_2O$	J. BUDDHUE; Pop. Astron. 1948 **56** 385 (HAWLEY)
34	Chateau-Renard	CaO = 0·14, S = 0·39	A. DUFRENOY; Comptes Rendus 1841 **13** 47
35	Cherokee Springs	MgO = 5·17, $Al_2O_3 = 12{\cdot}19$, S = 0, NiO = 15·40, all Fe as Fe_2O_3	S. PERRY; Pop. Astron. 1934 **42** 349 (KOUNTZ)

Table 1 (continued)

No.	*Name*	*Reasons Discarded*	*Reference*
36	Colby	$CaO = 0$	G. Merrill; Proc. U.S. Nat. Mus. 67, Article 2 1925 (Whitfield)
37	Cold Bokkeveld	Fe and S do not balance	F. Wohler and W. Haidinger; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1859 **35** 5 (Harris)
38	Collescipoli	$Al_2O_3 = 6{\cdot}43$, $S = 0$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 14 (Whitfield)
39	Collescipoli	$MgO = 0{\cdot}02$, $CaO = 0{\cdot}12$, $Na_2O = 10{\cdot}39$, $S = 7{\cdot}68$, All Fe as Fe	Trottarelli; Gazzetta Chim. Italiana 1890 **20** 611
40	Cuero	$Na_2O = 0{\cdot}27$, $H_2O = 1{\cdot}99$, $CO_2 = 0{\cdot}09$	V. Barnes; Univ. Texas Publ. 3945 1940 477 (Gonyer)
41	Cullison	$CaO = 0{\cdot}62$, $Na_2O = 1{\cdot}80$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 14 (Whitfield)
42	Cynthiana	$Al_2O_3 = 0{\cdot}22$	J. L. Smith; Amer. Jour. Sci. 1877 **14** 226
43	Danville	$K_2O > Na_2O$, Some FeS not included	J. L. Smith; Amer. Jour. Sci. 1870 **49** 90
44	Dhurmsala	$CaO = 0$, $Al_2O_3 = 0{\cdot}60$, $Cr_2O_3 = 2{\cdot}82$, $Na_2O = 0{\cdot}29$	S. Haughton; Proc. Roy. Soc. London 1866 **15** 214
45	Dokachi	$Al_2O_3 = 0{\cdot}44$	H. Clarke and H. Bowman; Min. Mag. 1911 **16** 44
46	Drake Creek	$CaO = 0{\cdot}70$, $NiO + CuO + SnO_2 = 2{\cdot}53$, $Cr_2O_3 = 1{\cdot}37$	E. Baumhauer; Ann. Phys. 1845 **66** 465
47	Dundrum	$Al_2O_3 = 0{\cdot}77$, $Cr_2O_3 = 1{\cdot}02$	S. Haughton; Proc. R. Soc. London 1866 **15** 214
48	Eichstadt	$CaO = 0{\cdot}74$	Gumbel; Sitz-ber. Math. Phys. Kl. Akad. Wissen. Munich 1878 **8** 14 (Schwager)
49	Eli Elwah	$Fe_2O_3 = 9{\cdot}18$	A. Liversidge; Jour. R. Soc. N.S.W. 1902 **36** 341
50	Elm Creek	$Fe_2O_3 = 12{\cdot}33$, no alkalis, $S = 0$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 15 (Whitfield)
51	El Perdido	$Fe_2O_3 = 17{\cdot}99$, $NiO = 0{\cdot}69$, $CoO = 2{\cdot}22$, $CaO = 0$	E. Ducloux; Rev. Fac. Cienc. Quim. Univ. Nac. La Plata 1929 **5** (Part 2) 1
52	Ensisheim	$NiO = 0{\cdot}46$	G. Prior; Min. Mag. 1921 **19** 163
53	Ensisheim	$MgO = 13{\cdot}13$, $Na_2O = 0{\cdot}38$	F. Crook; cited in [4] and [5]
54	Ergheo	$Na_2O + K_2O = 0{\cdot}13$, $S = 3{\cdot}46$, $CaO = 1{\cdot}08$	G. Boeris; cited in [5]
55	Erxleben	MnO listed as MgO?	Stromeyer; Ann. Phys. 1812 **42** 105
56	Farmington	$NiO = 0{\cdot}32$	G. Kunz and E. Weinschenk; Amer. Jour. Sci 1822 **43** 65 (Eakins)
57	Felix	$CaO = 5{\cdot}45$, $NiO + CoO = 1{\cdot}01$	G Merrill; Proc. U.S. Nat. Mus. 1902 **24** 193 (Fireman)
58	Fisher	No alkalis, $S = 0$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 16 (Whitfield)
59	Fisher	$Al_2O_3 = 6{\cdot}60$, no alkalis, $S = 0$, all Fe as Fe.	C. Berkey; Amer. Geol. 1897 **20** 316
60	Florence	$K_2O > Na_2O$, $Na_2O = 0{\cdot}39$	J. Lonsdale; Amer. Min. 1927 **12** 398 (Shannon)
61	Forsyth	$MgO = 9{\cdot}30$, $CaO = 5{\cdot}30$, no alkalis, FeS = 2–5%	C. Shepard; Amer. Jour. Sci 1848 **6** 402
62	Gilgoin No. 1	$MgO = 10{\cdot}80$, $CaO = 14{\cdot}95$, $Fe_2O_3 = 5{\cdot}72$	A. Liversidge; Jour. R. Soc. N.S.W. 1902 **36** 341
63	Gilgoin No. 7	All Fe as Fe, $NiO + CoO = 0{\cdot}48$ of sil. phase	J. Mingaye; Rec. Geol. Surv. N.S.W. 1916 **9** (Part 3) 166
64	Gualeguaychu	$NiO = 0{\cdot}35$	E. Ducloux; Anal. Mus. Arg. Cienc. Nat. Buenos Aires 1940 **40** 123
65	Harrison County	$CaO = 0{\cdot}77$, $Na_2O = 0{\cdot}40$, $K_2O > Na_2O$, $S = 0$	J. L. Smith; Amer. Jour. Sci. 1859 **28** 409
66	Hedeskoga	$NiO = 1{\cdot}04$, $Fe_2O_3 = 6{\cdot}89$, no alkalis	A. Hadding; Geol. Foren. Forhandl. 1924 **46** 383 (Sahlbom)
67	Hedjaz	$K_2O > Na_2O$	J. Couyat; Comptes Rendus 1912 **155** 916 (Pisani)
68	Heredia	$S = 0$	I. Domeyko; cited in [5]
69	Hermitage Plains	All Fe as Fe, $H_2O = 1{\cdot}74$	H. White; Rec. Geol. Surv. N.S.W. 1920 **9** 108

Table 1 (*continued*)

No.	*Name*	*Reasons Discarded*	*Reference*
70	Hessle	S = 0 and 0·37	A. NORDENSKJOLD; Ann. Phys. 1870 **141** 217
71	Hinojo	Fe_2O_3 = 16·53, NiO = 1·39, S = 0·54	E. DUCLOUX; Rev. Fac. Cienc. Quim. Univ. Nac. La Plata 1929 **5** (Part 2) 1
72	Holbrook	No alkalis	G. MERRILL; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 17 (WHITFIELD)
73	Homestead	Al_2O_3 = 0·64, CaO = 0	N. LEONARD; Amer. Jour. Sci. 1875 **10** 362 (J. L. SMITH)
74	Homestead	Al_2O_3 = 1·18, CaO = 1·39, K_2O = 0·57	C. GUMBEL; Sitz-ber. Math. Phys. Kl. Akad. Wissen. Munich 1875 **5** 326 (SCHWAGER)
75	Honolulu	CaO = 0	A. KUHLBERG; cited by O. BUCHNER, Ann. Phys. 1869 **136** 437
76	Hugoton	Fe_2O_3 = 18·14, NiO = 1·62, CoO = 0·24, H_2O + CO_2 = 4·14	H. NININGER; Trans. Kan. Acad. Sci. 1936 **39** 169 (HAWLEY)
77	Indarch	No alkalis, NiO = 0·55, CoO = 0·05	G. MERRILL; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 17 (WHITFIELD)
78	Isthilart	NiO = 1·24	E. DUCLOUX; Rev. Fac. Cienc. Quim. Univ. Nac. La Plata 1930 **6** (Part 2) 13
192	Jelica	Na_2O + K_2O = 0·12, CaO = 1·23	S. LOSANITSCH; Ber. Deutsch. Chem. Gesell. 1892 **25** 876
79	Jerome	NiO = 1·77, H_2O = 3·03	H. WASHINGTON; Amer. Jour. Sci. 1898 **5** 453
80	Kaba	Al_2O_3 = 5·38, Na_2O + K_2O = 0·30, CaO = 0·66	F. WOHLER; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1858 **33** 205
81	Kakowa	CaO = 0·96, S = 4·80	E. HARRIS; cited in [12]
82	Karoonda	Al_2O_3 = 5·55, Ni = 0·02	D. MAWSON; Trans. R. Soc. S. Australia 1934 **58** 1 (ALDERMAN)
83	Kesen	Al_2O_3 = 0, $K_2O > Na_2O$	K. JIMBO; cited in [8]
84	Klein-Wenden	$K_2O > Na_2O$, Na_2O = 0·28	C. RAMMELSBERG; Ann. Phys. 1844 **62** 463
85	Knyahinya	S = 0·81, K_2O = 0·66, Fe includes Ni	E. VON BAUMHAUER; Arch. Neer. Sci. Nat. 1872 **7** 146
86	Krahenberg	$K_2O > Na_2O$, Na_2O = 0·17, K_2O = 1·22	GUMBEL; Sitz-ber. Math. Phys. Kl. Akad. Wissen. Munich 1878 **8** 14 (KELLER)
87	Krahenberg	Al_2O_3 = 0·61	G. VON RATH; Ann. Phys. 1869 **137** 328
88	Kukschin	MgO = 6·22, NiO = 1·85, All Fe as FeO	I. ASTAPOWITSCH; Nature 1939 **143** 376 (PILIPENKO)
89	La Colina	Na_2O = 0, S = 0·64	E. DUCLOUX; Anal. Mus. Arg. Cienc. Nat. Buenos Aires 1925 **33** 287
90	L'Aigle	CaO = 4·60, K_2O = 0·86, S = 0·66	E. BAUMHAUER; Arch. Neer. Sci. Nat. 1872 **7** 154
91	Lake Brown	NiO = 0·32, Fe_2O_3 = 3·65, H_2O = 0·58	G. PRIOR; Min. Mag. 1929 **22** 155
92	Limerick	MnO = 5·50, Cr_2O_3 = 1·19	R. APJOHN; J. Chem. Soc. 1874 **27** 106
93	Lissa	CaO = 0·50, No alkalis, all Fe as Fe	KLAPROTH; cited in [8]
94	Little Piney	Al_2O_3 = 0·49, CaO = 0, no alkalis, S + P = 4·73	C. SHEPARD; Amer. J. Sci. 1840 **39** 254
95	Lixna	CaO = 0	C. KUHLBERG; cited by O. BUCHNER, Ann. Phys. 1869 **136** 437
96	Lixna	MgO = 10·8, CaO = 0, no alkalis	T. VON GROTTHUSS; cited in LAUGIER, Ann. Phys. 1823 **75** 264
97	Lixna	CaO = 0·5, no alkalis, S = 6·8, All Fe as Fe_2O_3	LAUGIER; Ann. Phys. 1823 **75** 264
98	Long Island	Cr_2O_3 = 6·33, NiO = 0·77, Na_2O = 0·25	H. NICHOLS; Field Mus. Nat. Hist. Pub. Geol. Series 1902 **1** 297
99	Lumpkin	CaO = 0·04	J. L. SMITH; Amer. J. Sci. 1870 **50** 339
100	Lundsgard	Fe: FeO wrong (see superior analysis ref.)	O. NORDENSKJOLD; Geol. Foren. Forhandl. Stockholm 1891 **13** 470
101	Makariwa	Fe_3O_4 = 3·48, Al_2O_3 = 0·16, Na_2O = 0·43	L. FLETCHER; Min. Mag. 1894 **10** 287

Table 1 (continued)

No.	*Name*	*Reasons Discarded*	*Reference*
102	Malotas	NiO = 0·88	E. Ducloux; Anal. Mus. Arg. Cienc. Nat. Buenos Aires 1940 **40** 130
103	Manbhoom	Na_2O = 0·44, Ni in silicate phase = 0·42	H. von Foullon; Ann. Naturhist. Hofmus. Vienna 1888 **3** 195
104	Mangwendi	NiO = 0·34	B. Lightfoot, A. Macgregor and E. Golding; Min. Mag. 1935 **24** 1
105	Marion	CaO = 1·17, Na_2O = 0·38	C. Rammelsberg; Monatsber. Berlin Akad. 1870 440
106	Mauerkirchen	Na_2O = 0·24, S = 0·70	F. Crook; cited in [4] and [5]
107	Maziba	No alkalis, Al_2O_3 = 0	R. Roberts; cited in Min. Abstr. 1949 **10** 400
108	McKinney	Al_2O_3 = 13·29, no alkalis	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** Fourth Memoir 12 (Whitfield)
109	Melrose	NiO = 1·22, Fe_2O_3 = 11·98, Na_2O = 0·29, SO_3 = 0·35	H. Nininger; Amer. Min. 1934 **19** 370
110	Melrose	Al_2O_3 = 5·20, 6·05, Na_2O = 1·68, 1·81, S = 0·22	C. Beck, R. Stevenson and L. La Paz; Pop. Astron. 1951 **59** 88
111	Menow	Al_2O_3 = 0	J. L. Smith; Amer. Jour. Sci. 1876 **12** 207
112	Middlesbrough	No alkalis, S = 0	W. Flight; Phil. Trans. R. Soc. 1882 **3** 885
113	Misshof	Al_2O_3 = 0·29, Na_2O = 3·94, K_2O = 1·13, MnO = 4·37	B. Doss; Neues Jahrb. Min. 1892 **1** 105
114	Mocs	Al_2O_3 = 0, MnO = 1·12, Mn = 0·57, Cr_2O_3 = 1·06	A Koch; Tschermak's Min. Pet. Mitt. 1883 **5** 243
115	Monroe	NiO + CoO = 0·46, no alkalis	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 20 (Whitfield)
116	Monroe	CaO = 0, no alkalis, MgO = 10·41	C. Shepard; Amer. J. Sci. 1850 **10** 127
117	Morland	NiO = 1·54, Fe_2O_3 = 13·86, SO_3 = 0·54, $CO_2 + H_2O$ = 2·24	H. Nininger; Trans. Kans. Acad. Sci. 1936 **39** 169 (Hawley)
118	Morven	NiO = 0·58	C. Hutton; Min. Mag. 1936 **24** 265
119	Motta di Conti	NiO = 5·37, Al_2O_3 = 0·42, Alkalis = 4·15, S = 0·50	Bertolino; Comptes Rendus 1868 **67** 873
120	Nerft	CaO = 0·05	O. Buchner; Ann. Phys. 1869 **136** 448 (Kuhlberg)
121	Ness County	No alkalis, Al_2O_3 = 8·26, S = 0	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 21 (Whitfield)
122	New Concord	CaO = 0·02, Al_2O_3 = 0·28, S = 0·12	J. L. Smith; Amer. J. Sci. 1861 **31** 87
123	New Concord	NiO = 0·81, Fe_2O_3 = 5·82, no alkalis, S = 0	Madelung; cited in [4]
124	New Concord	MgO = 8·87, Al_2O_3 = 5·32, CaO = 0·78, no alkalis	D. Johnson; Amer. J. Sci. 1860 **30** 103
125	Ngawi	Al_2O_3 = 0·78, Na_2O = 2·73, K_2O = 0·45, NiO = 1·57	E. von Baumhauer; Arch. Neer. Sci. Nat. 1884 **19** 175
126	Nogoya	All Fe as Fe_2O_3, Alkalis = 0·18	C. Friedheim; Sitz-ber. Akad. Wissen. Berlin 1888 **1** 345
127	Novo-Urei	Al_2O_3 = 0·60, no alkalis, S = 0·15	M. Jerofejeff and P. Latschinoff; cited in [8] p. 122
128	Ochansk	Al_2O_3 = 0, no alkalis, Fe for S uncertain	Tichomirow and Petrow; cited in G. Merrill, Mem. Nat. Acad. Sci. 1925 **14** Fourth Memoir 9
129	Ochansk	Al_2O_3 = 7·11, NiO = 0·56, SO_3 = 0·28	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** Fourth Memoir 8 (Whitfield)
130	Ogi	NiO = 0·30	E. Divers; Trans. Asiatic Soc. Japan 1882 **10** 199 (Shimidzu)
131	Ohaba	CaO = 0, Al_2O_3 = 0·28, S = 4·80	M. Hornes; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1858 **31** 79 (Bukeisen)
132	Orgueil	NiO = 2·61, Fe_2O_3 = 19·06, SO_3 = 2·33	S. Cloez; Comptes Rendus 1864 **59** 39
133	Orgueil	Al_2O_3 = 0·90, Fe_2O_3 = 7·78, FeS = 13·43	F. Pisani; Comptes Rendus 1864 **59** 134
134	Ornans	NiO = 2·88	F. Pisani; Comptes Rendus 1868 **67** 663
135	Otomi	No alkalis, all Fe as Fe	M. Hoshina; Jour. Geol. Geog. Japan 1925 **4**

Table 1 (*continued*)

No.	*Name*	*Reasons Discarded*	*Reference*
136	Paragould	All Fe as Fe_2O_3, S = 0	C. WYLIE; Pop. Astron. 1930 **38** 387 (ROY)
137	Parnallee	CaO = 0·56, NiO = 0·72, Na_2O = 1·91	E. PFEIFFER; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1863 **47** 460
138	Peck's Spring	Al_2O_3 = 7·12, NiO = 0·55, S = 0·83	G. MERRILL; Proc. U.S. Nat. Mus. 1929 **75** Article 16
139	Pickens County	CaO = 0·55, Fe_2O_3 = 10·69, Al_2O_3 = 5·83	S. MCCALLIE; Science 1909 **30** 772 (EVERHART)
140	Pillistfer	CaO = 0·48, Na_2O = 0·34	A. LACROIX; Bull. Soc. Franc. Min. 1905 **28** 70 (GREEWINGK and SCHMIDT)
141	Plainview	NiO = 0·77	G. MERRILL; Proc. U.S. Nat. Mus. 1917 **52** 419 (WHITFIELD)
142	Pultusk	Can't calculate bulk analysis accurately	C. RAMMELSBERG; Monatsber. Akad. Wissen. Berlin 1870 440
143	Pultusk	CaO = 0·28, Al_2O_3 = 1·08	G. VON RATH; Neues Jahrb. Min. 1869 80
144	Reliegos	MgO = 9·70, Al_2O_3 = 0·85, Cr_2O_3 = 5·75, no alkalis	J. LLARENA and C. ARANGO; Bol. Soc. Espanola Hist. Nat. 1950 **48** 303 (GARATA)
145	Renca	NiO = 1·13, Na_2O = 2·37, K_2O = 0·58	E. DUCLOUX; Rev. Fac. Cienc. Quim. Univ. Nac. La Plata 1929 **5** 111
146	Richardton	Fe_2O_3 = 3·48, FeS = 0	T. QUIRKE; J. Geol. 1919 **27** 431
147	Richmond	No alkalis	C. RAMMELSBERG; Monatsber. Akad. Wissen. Berlin 1870 **70** 440
148	Rochester	Al_2O_3 = 0·10, Na_2O = 0·58	J. L. SMITH; Amer. J. Sci. 1877 **14** 222
149	Rose City	NiO = 0·47, CoO = 0·07	E. HOVEY; Amer. Mus. Novitates No. 52 1922 1 (WHITFIELD)
150	Roy	Fe_2O_3 = 13·29, NiO = 1·27, Na_2O = 0·26, Fe = 0	H. NININGER; Pop. Astron. 1934 **42** 599 (HAWLEY)
151	Saint Mark's	Al_2O_3 = 0·64, S = 5·26	E. COHEN; Ann. S. African Mus. Cape Town 1906 **5** 15 (KLEIN)
152	Saint Mesmin	Alkalis = 3·13, CaO = 1·09, Cr_2O_3 = 1·48	F. PISANI; Comptes Rendus 1866 **62** 1326
153	Saline	Fe_2O_3 = 4·45, NiO = 0·74, Na_2O = 0·26, Cr_2O_3 = 1·25	H. NICHOLS and E. TILLOTSON; cited in [5]
154	San Carlos	NiO = 0·91, Na_2O = 0·13, MnO = 2·12, SnO_2 = 0·53	E. DUCLOUX; Notas Mus. La Plata 1942 **7** (Geol. No. 19) 123
155	Santa Isabel	NiO = 1·02	E. DUCLOUX; Rev. Fac. Cienc. Quim. Univ. Nac. La Plata 1926 **4** (Part 1) 23
156	Sauguis	Na_2O = 0, CaO = 0·50, Al_2O_3 = 0	DAUBREE; Comptes Rendus 1868 **67** 873
157	Schonenberg	Al_2O_3 = 5·57, Na_2O = 2·20, K_2O = 0·73, MgO = 13·81	GUMBEL; Sitz-ber. Math. Phys. Kl. Akad. Wissen. Munich 1878 **8** 14 (SCHWAGER)
158	Searsmont	Al_2O_3 = 0·81, CaO = 0	J. L. SMITH; Amer. J. Sci. 1871 **2** 200
159	Selma	Fe = 0, NiO = 1·45, Fe_2O_3 = 18·15, Na_2O = 3·96, S = 0·19	G. MERRILL; Mem. Nat. Acad. Sci. 1925 **14** First Memoir 21 (WHITFIELD)
160	Seres	K_2O = 2·08, $K_2O > Na_2O$, Mn_2O_3 = 2·40, Fe and FeS = 0	J. BERZELIUS; Ann. Phys. 1829 **16** 611
161	Sharps	NiO = 0·42, SO_3 = 1·26	T. WATSON; Proc. U.S. Nat. Mus. 1925 **64** 1
162	Shytal	NiO = 0·86	T. HEIN; Sitz-ber. Math.-Natur. Cl. Akad. Wissen. Vienna 1866 **54** (Abt. 2) 558
163	Soko-Banja	CaO = 0, Al_2O_3 = 0, Na_2O = 0·25	S. LOSANITCH; Ber. Deutsch. Chem. Gesell. 1878 **11** 96
164	Staroye Boriskino	All Fe as Fe_2O_3, H_2O = 11·68	L. KVASHA; cited in Min. Abstr. 1949 **10** 516
165	Stavropol	NiO = 3·81, SnO_2 = 1·10	H. ABICH; Bull. Akad. Sci. St. Petersburg 1860 **2** 403 and 433
166	Tadjera	No alkalis	S. MEUNIER; Comptes Rendus 1868 **66** 518

Table 1 (*continued*)

No.	*Name*	*Reasons Discarded*	*Reference*
167	Takenouchi	$Al_2O_3 = 0$, $Cr_2O_3 = 1{\cdot}07$	Lindner and Lance; Sitz-ber. Akad. Wissen. Berlin 1904 **1** 981
168	Tenham	Incomplete—Residue = 5·2%	L. Spencer; Min. Mag. 1937 **24** 437
169	Tennasilm	Alkalis = 2·24, S = 0·62, Fe for S uncertain	G. Schilling; cited in [8] and [9]
170	Tilden	$NiO = 0{\cdot}99$, $CaO = 0{\cdot}91$	A. Crook and O. Farrington; Trans. Illinois Acad. Sci. 1929 **22** 442 (Nichols)
171	Timochin	$CaO = 0{\cdot}75$, no alkalis, Fe for S uncertain	Klaproth; Ann. Phys. 1809 **33** 210
172	Tjerebon	$CaO = 0{\cdot}80$, $K_2O = 0{\cdot}43$	W. Gisolf; cited in Min. Abstr. 1927 **21** 256
173	Tomakovka	No alkalis	P. Tchirvinsky; Bull. Soc. Franc. Min. 1921 **44** 155
174	Tomatlan	$SO_3 = 5{\cdot}20$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** Fourth Memoir 3
175	Tostado	$Fe_2O_3 = 6{\cdot}05$, $NiO = 1{\cdot}64$, $CaO = 0{\cdot}81$, $K_2O = 0{\cdot}89$	E. Ducloux; Notas Mus. La Plata 1945 **10** (Geol. No. 41) 165
176	Travis County	$NiO = 0{\cdot}52$	L. Eakins; Bull. U.S. Geol. Surv. 1891 **78** 91
177	Trenzano	$Na_2O = 1{\cdot}84$, $K_2O = 1{\cdot}47$	G. Curioni; cited in [10] p. 190
178	Troup	$CoO = 0{\cdot}42$, $MgO = 4{\cdot}30$, $Na_2O = 3{\cdot}86$, $S = 6{\cdot}21$	J. Udden; Proc. U.S. Nat. Mus. 1922 **59** 471 (Schoch and Stullken)
179	Tulia	$NiO = 0{\cdot}72$, $Al_2O_3 = 5{\cdot}91$, $K_2O = 0{\cdot}50$	C. Palache and J. Lonsdale; Amer. J. Sci. 1927 **13** 353
180	Uden	$NiO = 0{\cdot}29$, $S = 0{\cdot}26$	E. Baumhauer and F. Seelheim; Ann. Phys. 1862 **116** 184
181	Ulmiz	All Fe as Fe_2O_3	E. Hugi; Mitt. Naturfors. Gesell. Bern. 1929 34 (Quervain)
182	Utrecht	$NiO + MnO = 0{\cdot}61$	E. Baumhauer; Ann. Phys. 1845 **66** 465
183	Vernon County	$Al_2O_3 = 0$	J. L. Smith; Amer. J. Sci. 1876 **12** 207
184	Waconda	$NiO = 0{\cdot}74$	G. Merrill; Mem. Nat. Acad. Sci. 1925 **14** Fourth Memoir 14 (Whitfield)
185	Waconda	$CaO = 0$	J. L. Smith; Amer. J. Sci. 1877 **13** 211
186	Warrenton	$NiO = 1{\cdot}16$, $Na_2O = 0{\cdot}23$, $Al_2O_3 = 0{\cdot}13$	J. L. Smith; Amer. J. Sci. 1877 **14** 223
187	Weston	All Fe as Fe_2O_3, no alkalis, $Cr_2O_3 = 2{\cdot}33$	Warden; Ann. Chim. 1810 **73** 293
188	Yandama	$Al_2O_3 = 7{\cdot}36$, $H_2O = 2{\cdot}59$	A. Alderman; Rec. S. Australian Mus. 1936 **5** 537
189	Yonozu	$Fe_2O_3 = 6{\cdot}91$, $S = 0{\cdot}22$, $MnO = 0{\cdot}95$	C. Beck and R. Stevenson; Amer. J. Sci. 1951 **249** 815
190	Zaborzika	All Fe as Fe_2O_3, no alkalis, $Al_2O_3 = 0{\cdot}75$	Laugier; Ann. Phys. 1823 **75** 264
191	Zavid	$CaO = 4{\cdot}60$, $K_2O = 0{\cdot}41$	C. Hodlmoser; Tschermak's Min. Pet. Mitt. 1899 **18** 513
192	Jelica	(Listed alphabetically)	

Table 2. Sup

No.	*Name*	*Type*	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	*Silicate*	Fe	Ni
* 1	Albareto	*Cc*	40·38	24·88	15·41	3·22	2·60	1·23	0·30	0·28	0·14	Tr		88·44	4·49	0·7
2	Allegan	*Cc*	34·95	21·99	8·47	2·55	1·73	0·66	0·23	0·53	0·18	0·08	0·27	71·64	21·09	1·8
* 3	Baroti	*Cw*	39·64	24·71	14·39	2·40	1·79	0·91	0·04	0·18	Tr	0·16	0·25	84·47	7·70	1·1
* 4	Beaver Creek	*Cc*	37·93	23·35	9·98	1·90	1·62	0·81	0·12	0·42	0·21	0·07	0·25	76·66	16·04	1·5
* 5	Benld	*Cga*	36·27	23·80	11·58	2·86	1·92	0·76	0·20	0·10	0·31	0·10	0·27	78·17	17·31	1·6
6	Benoni	*Cgb*	36·00	22·91	9·82	2·51	1·84	1·05	0·05	0·28	0·30	0·09	0·21	75·06	17·16	1·6
* 7	Bjurbole	*Cc*	41·06	25·75	13·17	2·55	1·82	1·24	0·32	0·59	0·12		0·32	86·94	6·87	0·7
* 8	Bowden	*Cck*	36·35	23·01	10·08	2·88	2·21	0·76	0·11	0·32	0·24	0·12	—	76·08	16·10	1·4
9	Cape Girardeau	*Cc*	35·71	23·84	11·30	2·28	1·38	0·86	0·11	0·47			0·29	76·24	16·46	1·3
*10	Chandakapur	*Cib*	38·02	21·31	19·54	4·17	2·42	1·26	0·29	0·35				87·36	6·40	[6
11	Chantonnay	*Cgb*	37·38	25·37	14·98	2·53	1·41	[1·14]		0·66	0·27			83·74	6·73	1·1
*12	Cobija	*Ck*	37·06	23·35	11·21	2·81	2·55	0·72	0·14	0·30	0·24	0·13		78·51	12·95	1·2
13	Collescipoli	*Cc*	36·31	23·42	5·94	3·67	1·18	1·31	0·24	0·60	0·31	0·18	Tr	73·16	18·30	1·5
*14	Coon Butte	*Cib*	42·62	26·55	15·46	1·69	0·96	0·40	0·12	0·05		Tr		87·85	8·09	1·1
*15	Cronstad	*Cga*	37·24	23·61	8·06	2·41	1·45	0·67	0·07	0·37	0·04	0·30	0·25	74·47	17·57	1·6
16	Crumlin	*Cg*	40·73	25·36	13·24	2·14	2·04	1·07	0·11	0·60	0·27	0·17	0·26	85·99	7·75	1·1
*17	Daniel's Kuil	*Cek*	38·47	21·63	0·23	1·78	1·03	0·64	0·15	0·23	0·02	0·12	Tr	64·30	23·70	1·8
18	Djati-Pengilon	*Ck*	34·56	21·07	13·75	1·46	1·17	0·45	0·03	0·16	Tr			72·65	18·89	2·3
*19	Ekeby[1]	*Cg*	35·33	22·91	10·88	1·81	1·99	0·97	0·20	0·46	0·25	0·22	0·29	75·31	16·93	1·7
*20	Elsinora	*Cga*	35·47	25·21	9·29	2·02	1·56	0·82	0·01	0·34	0·07	0·05	0·10	74·94	18·23	1·3
21	Estacado	*Cka*	35·82	22·74	12·45	3·60	2·99	2·07	0·32	Tr	Tr	Tr		79·99	14·68	1·6
*22	Forest City	*Ccb*	35·62	23·94	8·11	2·08	1·42	0·81	0·06	0·10	Tr		Tr	72·14	19·63	1·3
*23	Forksville	*Cc*	38·16	26·25	18·58	3·00	1·35	0·49	0·26	0·09	Tr		0·23	88·41	6·60	0·9
24	Girgenti	*Cwa*	39·81	24·61	16·86	1·44	1·70	1·38		0·81	Tr			86·61	7·25	1·0
25	Gnadenfrei	*Cc*	32·11	17·03	14·88	1·60	2·01	0·70		0·57	Tr		Tr	68·90	21·90	3·9
26	Gopalpur	*Cc*	37·44	19·72	11·94	2·52	1·60	0·62	0·21	Tr	0·26			74·31	17·93	1·8
27	Grossliebenthal	*Cwa*	39·57	22·97	12·92	2·45	2·28	1·30	0·45	0·88	0·53		0·21	83·56	6·80	1·3
28	Hendersonville	*Cc*	46·06	28·62	10·89	2·20	2·13	0·96	0·10	0·58				91·54	2·37	0·2
29	Hessle	*Cc*	36·83	23·21	10·87	2·38	1·80	0·94		0·05	0·42			76·50	16·81	2·1
*30	Homestead	*Cgb*	39·27	24·88	12·42	2·10	1·78	0·92	0·13	0·32	0·08		0·26	82·16	9·71	1·1
31	Hvittis[2]	*Cek*	41·53	23·23	0·34	1·55	0·74	1·26	0·32	0·15				69·12	20·04	1·9
32	Kernouve	*Cka*	32·95	23·68	11·70	3·19	1·89	[1·41]		Tr				74·82	18·50	1·5
*33	Khairpur	*Cek*	42·64	23·09	2·72	1·76	1·46	0·80	0·10	0·26		—	Tr	72·83	16·83	1·2
34	Khetri	*Cgb*	35·17	23·80	10·67	1·77	2·37	0·87	Tr	0·40				75·05	17·63	1·2
*35	Kimble County[3]	*Ca*	37·33	23·24	14·98	3·06	1·67	0·67	0·20	0·17	0·14	0·11	0·19	81·76	12·63	0·8
*36	Knyahinya	*Cg*	30·93	23·36	9·96	2·46	3·34	0·58	0·02	0·08	0·61	0·06	0·06	71·46	20·77	1·8
*37	Lanzenkirchen	*Cw*	39·86	23·58	12·61	4·26	1·66	2·29	0·27	0·44	0·07	0·07	0·11	85·22	8·16	1·1
*38	Launton	*Cia*	39·70	24·89	13·00	2·40	2·09	1·01	0·09	0·31	0·29	0·18	0·15	84·11	7·74	1·2
39	Lesves	*Cg*	39·46	22·75	15·82	3·33	1·54	1·05	0·09	1·02				85·06	8·44	1·3
*40	Limerick	*Cga*	36·88	23·32	7·79	1·50	1·86	0·95	0·14	0·59	0·15		0·27	73·45	18·48	1·6
41	Linum	*Cw*	43·05	25·72	1·32	2·44	3·49	1·39	0·26	0·31	0·20			78·18	15·83	0·7
*42	Lissa	*Cw*	35·43	24·16	15·41	1·85	2·48	1·36	0·38	0·06	0·92	0·02	0·18	82·25	9·21	0·8
*43	Lundsgard[4]	*Cg*	38·23	24·29	14·97	2·42	2·43	1·42	0·38	0·49	0·27	0·19	0·28	85·37	5·95	1·0
44	Mauerkirchen	*Cw*	38·14	21·73	25·70	2·51	2·27	1·00	0·48	0·39				92·22	[2·66]	
45	McKinney	*Cs*	39·77	23·82	12·82	3·42	1·79	0·75	0·22	0·51	0·31	0·14	0·27	83·82	7·81	0·7
*46	Merua	*Cg*	36·88	23·61	7·45	2·53	1·82	0·59	0·07	0·37	0·18	0·13	0·29	73·92	18·17	1·8
47	Meuselbach[5]	*Ccka*	38·78	24·76	16·11	2·88	2·08	1·54	Tr	0·23				86·38	6·66	1·0
48	Mezel	*Cga*	39·45	24·55	14·99	2·06	1·50	0·84	Tr	0·66	0·37	0·37	0·28	85·07	5·32	0·6
*49	Mezo-Madaras	*Cgb*	36·79	24·10	15·09	3·41	1·68	1·76	Tr	0·54	0·18			83·55	8·40	1·6
50	Modoc	*Cwa*	44·13	26·45	12·28	2·47	1·74	0·44	Tr		0·10			87·61	6·56	0·6
*51	Moorleah	*C*	40·39	25·89	14·34	2·81	1·49	1·32	0·04		Tr			86·28	6·68	0·8
*52	Mount Browne	*Cc*	34·81	23·35	12·29	2·27	2·24	1·17	0·24	0·02				76·39	15·77	1·7
*53	Narellan	*Cg*	38·45	21·11	16·43	2·20	1·56	0·60	0·24	0·44	0·48	0·13	0·41	82·05	8·58	1·2
54	Oakley	*Ck*	36·55	23·47	10·21	1·91	2·41	0·78	0·20	0·52	0·35	0·14	0·30	76·84	15·15	1·8
55	Oesede	*Cc*	35·57	23·24	7·99	2·71	2·96	1·32	0·40					74·19	18·17	1·9
56	Ojuelos Altos	*Ci*	40·02	25·34	11·34	2·77	2·49	0·76	0·23			—	0·34	83·29	8·17	1·1
57	Olivenza	*Cc*	40·73	25·16	20·74	2·30	2·09	0·92	0·33	0·14	0·15	—	0·19	92·75	0·77	0·4
58	Olmedilla de Alarcon	*Cwb*	36·92	23·59	9·39	2·52	2·16	0·87	0·19	0·38	0·26	—	0·31	76·59	17·06	1·5
59	Orvinio[6]	*Co*	37·41	22·90	7·98	2·26	2·32	1·21	0·28					74·36	18·75	2·5
60	Oubari[7]	*Cgb*	38·70	24·80	19·50	2·15	1·90	0·83	0·19	0·30	0·39	0·26	0·25	89·27	1·80	0·6
*61	Perpeti	*Cw*	39·09	25·11	14·98	1·35	1·88	1·17	0·14	0·65	0·27	0·16	0·27	85·07	7·01	1·1
62	Phu-Long	*Cck*	36·28	23·23	11·88	3·28	2·21	0·71	0·21	0·11	0·13		0·21	78·25	15·81	1·2
63	Phuoc-Binh	*Cg*	39·66	24·73	13·95	2·13	2·41	0·74	0·10		0·32		0·35	84·39	7·32	1·8
*64	Plantersville[8]	*Cia*	35·87	23·57	12·01	2·18	1·97	1·05	0·12	0·03	0·18	—	0·05	77·03	17·06	1·9
65	Prambachkirchen	*Cw*	38·51	23·46	12·45	3·88	2·24	1·16	0·23	0·05	1·21	0·12	0·32	83·63	8·32	0·8
66	Rakovka	*Ci*	38·87	24·60	13·70	2·66	2·36	2·07	0·37	0·55	0·24			85·42	5·67	1·4
*67	Rangala	*Cwa*	40·02	24·67	15·03	2·27	2·07	0·61	0·14	0·29	0·12	0·08	0·26	85·56	8·26	1·0
*68	Rich Mountain	*Cia*	41·28	26·43	10·94	2·60	2·50	0·68	0·16				0·07	84·66	7·07	0·7
*69	Rosebud	*Csa*	34·28	23·77	17·30	3·53	1·80	0·41	0·06	0·14	0·15	—	0·09	81·53	13·31	1·2
70	Saint Christophe	*Cw*	39·33	25·90	13·66	2·15	1·51	0·51	0·18	0·39				83·63	7·79	1·6
71	Saint Denis-Westrem	*Cca*	40·20	25·08	15·54	2·54	2·00	0·99	Tr	0·90	Tr			87·25	7·21	1·2
72	Saint Michel	*Cw*	39·52	24·60	13·44	3·31	1·64	1·32	0·13	0·56	0·41	0·02		84·95	7·84	1·1
73	Saint-Sauveur[9]	*Cek*	33·40	17·00	0·21	3·29	1·12	0·96	0·21				0·17	56·36	25·73	1·6
74	Salt Lake City	*Cgb*	36·29	23·17	11·98	1·96	1·89	0·85	0·06	0·42			0·27	76·89	15·67	1·3
75	Saratov	*Cc*	41·02	25·09	13·01	1·66	2·26	0·50	0·09	0·66	0·36	0·11	0·68	85·44	7·25	0·9
*76	Sazovice	*Cga*	38·57	23·32	14·97	3·09	2·38	[0·86]			0·70	0·06	0·05	84·00	7·82	1·1
*77	Seldebourak	*Cc*	35·30	24·15	13·98	1·35	1·80	0·65	0·28	0·23	0·23	0·13	0·25	78·35	15·27	1·4

ses of chondrites

Fe	S	FeS	P	H_2O+	H_2O-	*Total*	Fe(M) / Fe(FeS)	Fe *Silicate Phase*	Fe *Total*	Group	*Accessories*	*Sp. Gr.*	*No.*
5·18	2·17	5·95	Tr	[0·28]		99·90	8·27	11·97	20·24	*L*	C = Tr		* 1
5·21	1·84	5·05		0·19	0·06	100·00	24·30	6·58	30·88	*H*	Cu = 0·01, Li_2O = Tr	3·90	2
4·32	2·47	6·79		[0·17]		100·36	12·02	11·18	23·20	*L*		3·54	* 3
5·21	1·84	5·05		[0·28]		99·68	19·25	7·75	27·00	*H*	Cu = 0·01, Cl = Tr		* 4
4·60	0·92	2·52	0·02	[0·08]		99·84	18·91	9·00	27·91	*H*	Cu = 0·02	3·69	* 5
5·69	2·11	5·80		[0·20]		100·06	20·85	7·63	28·48	*H*	C = 0·05	3·70	6
5·45	1·99	5·44				100·07	10·32	10·23	20·55	*L*			* 7
5·76	2·15	5·91		[0·27]		99·91	19·86	7·83	27·69	*H*		3·39	* 8
5·63	2·08	5·71		[0·48]		100·33	20·09	8·78	28·87	*H*	Cu = 0·01	3·67	9
4·13	1·79	4·92	0·16			99·76	9·53	15·18	24·71	*L*	Cu = Tr	3·53	*10
3·92	2·24	6·16				97·79	10·65	11·64	22·29	*L*			11
5·68	2·10	5·78		[0·45]		98·99	16·63	8·71	25·34	*H*		3·58	*12
5·96	2·27	6·23		0·07	0·06	99·48	22·26	4·62	26·88	*H*			13
1·36	0·78	2·14	0·11	[0·31]		99·66	9·45	12·01	21·46	*L*	C, Cu, Sn = Tr	3·47	*14
5·29	1·88	5·17		[0·34]		99·41	20·86	6·26	27·12	*H*		3·61	*15
3·34	1·91	5·25				100·22	11·09	10·29	21·38	*L*		3·55	16
5·15	2·94	8·09		[0·34]		99·89	28·85	0·18	29·03	[*H*]	C = 0·32, CaS = 0·86, Cr_2S_3 = 0·29	3·66	*17
3·24	1·86	5·10				99·06	22·13	10·68	32·81	*H*		3·75	18
3·33	1·91	5·24		0·13	0·03	99·37	20·26	8·45	28·71	*H*			*19
3·04	1·74	4·78		[0·41]		99·69	21·27	7·22	28·49	*H*	CuO "present"	3·59	*20
2·39	1·37	3·76	0·15			100·26	17·07	9·67	26·74	*H*	C = "present," Cu = Tr	3·61	21
3·93	2·26	6·19				99·39	23·56	6·30	29·86	*H*			*22
1·99	1·14	3·13				99·09	8·59	14·44	23·03	*L*	Cu = Tr		*23
3·15	2·05	5·20				100·11	10·40	13·10	23·50	*L*		3·55	24
3·26	1·87	5·13				99·85	25·16	11·56	36·72	[*H*]		3·71	25
4·03	1·74	4·77				98·91	20·96	9·28	30·24	*H*			26
2·74	2·72	7·46	0·02	[0·10]		99·34	11·54	10·04	21·58	*L*	Cl = 0·04	3·58	27
2·80	1·61	4·41	0·01			98·55	5·17	8·46	13·63	[*L*]			28
3·27	1·88	5·15	0·15			100·84	20·08	8·45	28·53	*H*	C = Tr, Cl = 0·04, CuO + ZnO = 0·02	3·70	29
5·97	2·28	6·25		[0·47]		99·87	13·68	9·65	23·33	*L*			*30
4·62	2·65	7·27	0·08			99·96	24·66	0·26	24·92	[*H*]	CaS = 0·86, Cr_2S_3 = 0·56		31
5·75	2·15	5·90				100·77	22·25	9·09	31·34	*H*	Cu = Tr	3·75	32
4·53	2·59	7·12		[0·20]		99·39	21·36	2·11	23·47	[*H*]	C = 0·41, CaS = 0·34, Cr_2S_3 = 0·20	3·49	*33
4·07	1·76	4·83	0·12			101·20	20·70	8·29	28·99	*H*	Cr = 0·10, Loss = 2·00	3·68	34
3·37	1·37	3·74	Tr	[0·43]		99·47	15·00	11·64	26·64	*L*	Cu = 0·01	3·43	*35
4·85	2·21	6·06	Tr		0·04	100·22	24·62	7·74	32·36	*H*	Cr, Cu, Mn = Tr		*36
1·32	1·90	5·22		[0·05]		99·84	11·48	9·80	21·28	*L*	Cl = 0·03	3·49	*37
2·80	2·18	5·98		[0·42]		99·62	11·54	10·10	21·64	*L*		3·35	*38
1·92	2·25	6·17				101·15	12·36	12·29	24·65	*L*		3·58	39
4·57	2·03	5·60		[0·68]		99·99	22·05	6·05	28·10	*H*			*40
5·23	1·85	5·08	0·07	[0·12]		99·99	19·06	1·03	20·09	[*H*]		3·54	41
4·91	2·82	7·73	Tr		0·03	100·14	14·12	11·97	26·09	*L*	C, Cr, Cu, Mn = Tr		*42
4·00	2·87	7·87		0·10	0·07	100·38	10·95	11·63	22·58	*L*			*43
3·54	2·09	5·73	0·14			100·75	6·30	19·97	26·27	[*L*]		3·46	44
4·11	2·36	6·47		0·44	0·14	99·51	11·92	9·96	21·88	*L*			45
3·61	2·07	5·68		[0·35]		100·05	21·78	5·79	27·57	*H*		3·73	*46
4·30	2·47	6·77				100·99	10·96	12·52	23·48	*L*		3·47	47
4·08	2·34	6·42		[1·03]		98·67	9·40	11·65	21·05	*L*	Insol. in Metal Phase = 0·19	3·50	48
3·97	2·27	6·24				99·88	12·37	11·72	24·09	*L*			*49
2·40	1·38	3·78	0·05			98·71	8·96	9·54	18·50	*L*		3·54	50
4·98	2·29	6·27	Tr	[0·05]		100·20	10·66	11·14	21·80	*L*	Cl = Tr	3·51	*51
3·52	2·02	5·54	0·11			99·96	19·29	9·55	28·84	*H*	C = 0·11		*52
4·62	2·66	7·28		[0·02]		99·16	13·20	12·77	25·97	*L*		3·45	*53
3·88	2·23	6·11		0·15	0·06	100·32	19·03	7·93	26·96	*H*			54
5·66	2·11	5·77	Tr			100·03	21·83	6·21	28·04	*H*			55
4·30	2·46	6·76			0·09	99·47	12·47	8·81	21·28	*L*			56
3·82	2·19	6·01	—			99·96	4·59	16·11	20·70	[*L*]	Mn = Tr	3·45	57
2·97	1·69	4·66			0·09	100·00	20·03	7·30	27·33	*H*		3·71	58
3·47	1·99	5·46				101·16	22·22	6·20	28·42	*H*		3·64	59
4·48	2·56	7·04		0·22	0·24	99·28	6·28	15·15	21·43	[*L*]			60
5·88	2·22	6·10				99·55	10·89	11·64	22·53	*L*	CaS = 0·14		*61
2·87	1·65	4·52		[0·06]		99·87	18·68	9·23	27·91	*H*		3·66	62
4·04	2·32	6·36				99·90	11·36	10·84	22·20	*L*		3·56	63
2·53	1·45	3·98	Tr			100·06	19·59	9·33	28·92	*H*	Cu = Tr	3·71	*64
4·88	2·80	7·68		—		100·59	13·20	9·67	22·87	*L*	Cl = 0·01, C Cu = Tr	3·58	65
2·91	2·25	6·16	0·12			99·25	9·58	10·64	20·22	*L*	C = 0·13, Mn = Tr	3·58	66
4·26	1·86	5·12		[0·03]		100·11	11·52	11·68	23·20	*L*		3·62	*67
2·47	1·42	3·89				96·39	9·54	8·50	18·04	*L*	C = 0·01		*68
2·17	1·25	3·42	Tr	[0·07]		99·64	15·48	13·44	28·92	[*L*]	Cu = Tr	3·59	*69
4·38	2·52	6·90	Tr			100·10	12·17	10·61	22·78	*L*	C = Tr		70
3·69	2·12	5·81				101·63	10·90	12·07	22·97	*L*		3·29	71
3·87	2·22	6·09	0·08			100·26	11·71	10·44	22·15	*L*	Cu = 0·01	3·56	72
9·13	5·24	14·37		[0·09]		99·74	34·86	0·16	35·02	[*H*]	C = 0·10, CaS = 1·15, Cr_2S_3 = 0·15 Mn = 0·05	3·66	73
3·52	2·03	5·55		[0·94]		100·54	19·19	9·31	28·50	*H*	Cu = 0·01	3·66	74
4·00	2·30	6·30		[0·04]		100·08	11·25	10·11	21·36	*L*	Cl = 0·01, Br = $4·2 \times 10^{-5}$		75
4·41	2·53	6·94	Tr		0·08	100·16	12·23	11·63	23·86	*L*	C, Cr, Cu, Mn = Tr		*76
2·93	1·68	4·61		0·08		99·94	18·20	10·86	29·06	*H*		3·69	*77

Table 2

No.	*Name*	*Type*	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	*Silicate*	Fe	Ni	Co
78	Shelburne	*Cgα*	39·19	26·24	15·16	2·15	1·75	0·73	0·22	0·62	0·12			86·18	7·90	0·78	0·04
79	Soko-Banja	*Cc*	41·45	25·63	17·73	2·12	1·92	0·85	0·07	0·36	0·05	0·10	0·24	90·52	3·17	1·06	0·09
*80	Stalldalen	*Cgb*	35·71	23·16	8·10	2·11	1·61	0·62	0·15	0·40	0·25		0·30	72·41	18·85	1·77	0·17
*81	Strathmore	*Ci*	40·32	24·96	13·30	2·57	1·84	0·90	0·11	0·44	0·29	0·14	0·23	85·10	7·31	1·26	0·05
82	Suwahib	*Cs*	38·48	21·25	10·16	4·42	1·90	1·33	0·25		0·28	0·20		78·27	14·09	0·96	0·12
*83	Tabor	*Ccb*	33·25	24·32	11·26	2·20	2·89	0·95	0·07	0·08	0·54	0·07	0·14	75·77	15·63	1·24	0·11
84	Tanezrouft	*Cg*	37·16	24·52	10·10	1·99	1·87	0·98	0·29	0·32	0·18	0·32	0·27	78·00	15·31	1·36	0·04
85	Tieschitz	*Cc*	40·23	20·55	19·48	1·93	1·54	1·53			0·32		0·22	85·80	7·39	1·31	
86	Tourinnes-la-Grosse	*Cw*	37·47	24·40	14·12	3·65	2·61	[2·26]		0·48	Tr			84·99	7·20	1·30	
87	Tuan Tuc	*Cg*	40·35	25·19	14·93	2·97	1·99	0·67	0·21	0·14	0·21		0·29	86·95	6·03	0·78	0·02
88	Varpaisjarvi	*Cw*	39·28	23·94	12·68	4·32	1·88	0·83	0·23	0·66	0·14	0·17	0·28	84·41	7·58	1·09	0·11
89	Vavilovka	*"CAm"*	39·96	25·32	18·08	1·63	1·80	1·61	0·26	0·15	0·77	—	—	89·58	1·79	0·93	0·06
*90	Warbreccan	*Cwa*	39·86	24·75	14·11	1·71	2·01	0·92	0·06	0·41	0·39	0·21	0·26	84·69	6·54	1·15	0·08
91	Warrenton	*Cco*	34·82	23·57	24·34	2·18	2·17	0·69	0·23	0·58	0·20	0·15	0·20	89·13	4·02	1·43	0·09
*92	Wittekrantz	*Cx*	41·12	25·40	15·16	2·54	2·12	1·16	0·14	0·36	0·15	0·17	0·16	88·48	7·10	1·11	0·02
*93	Zebrak	*Cc*	30·32	22·64	11·28	2·01	2·15	1·08	0·23	0·06	0·75	0·04	0·08	70·64	21·79	2·26	0·15
*94	Zemaitkiemis	*Cgb*	40·30	22·33	12·04	3·08	2·30	2·06	0·26		0·22	0·05	0·30	82·94	11·42	0·80	
	Average:[10]																
	L Group	(53)	39·49	24·55	14·97	2·61	1·96	1·04	0·18	0·43	0·27	0·11	0·24	85·85	7·04	1·06	0·07
	H Group	(41)	36·17	22·93	9·26	2·36	1·95	0·91	0·17	0·27	0·23	0·11	0·17	74·53	17·76	1·68	0·10
	All chondrites	(94)	38·04	23·84	12·45	2·50	1·95	0·98	0·17	0·36	0·25	0·11	0·21	80·86	11·76	1·34	0·08

* Original values of Fe, Ni, FeO, Fe_2O_3, and NiO given in Table 3.

(1) Total composition calculated incorrectly in original reference. Bulk analysis recalculated here from silicate and metal phase compositions.

(2) CaO and Cr_2O_3 were subtracted from the oxides as given to form the sulphides, as discussed in text of reference.

(3) FeO given incorrectly in calculated total analysis in original reference.

(4) S, and O correction for S, miscalculated in total analysis in original. FeS in norm also incorrect.

(5) Average of two analyses.

(6) Average of (1) rounded pebble like masses and (2) black matrix.

(7) Original misstates Fe_2O_3 for FeO.

(8) Original calculation of bulk analysis neglects to include Fe from FeS.

(9) Cr and Ca in analysis were calculated as sulphides in accordance with the analyst's statements.

(10) Iron constituents from No. 44 not included in averages because of Ni content. Note that averaging P into P_2O_5 column (except when both P and P_2O_5 are reported) gives averages for low group, high group, and total of 0·22, 0·18, and 0·20% P_2O_5 respectively. Though the differences are not significant this is probably the correct procedure.

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Table 1 lists the 192 analyses of chondrites which we have discarded, the reasons for their elimination, and the original reference. In the few cases in which the original reference was not available the source from which we took the analysis is given. The notation "Fe for S uncertain" means that the statement of the analysis gives no indication as to the location of the iron occurring in iron sulphide. In some cases the notation "all Fe as Fe," indicates that no breakdown of total iron into FeO and metallic iron was made. There are perhaps some 30 other analyses we have discarded which are not listed. These are to be found mainly in compilations [4] and [10], and consist of analyses which generally lack all of the following: CaO, Al_2O_3, Na_2O, K_2O, and minor oxides, and which are so obviously bad that we have felt justified in eliminating them completely from

ntinued)

Fe	S	FeS	P	H_2O+	H_2O-	*Total*	Fe(M) + Fe(FeS)	Fe *Silicate Phase*	Fe *Total*	*Group*	*Accessories*	*Sp. Gr.*	*No.*
2·80	1·61	4·41	0·06			99·37	10·70	11·78	22·48	*L*			
3·17	1·81	4·98		[0·17]		99·99	6·34	13·78	20·12	[*L*]		3·50	78
3·95	2·27	6·22	0·01			99·47	22·80	6·29	29·09	*H*	Cl = 0·04	3·50	79
4·00	2·29	6·29		[0·17]		100·21	11·31	10·33	21·64	*L*	Cl = 0·03	3·74	*80
3·45	1·98	5·43	—			98·87	17·54	7·89	25·43	*H*		3·53	*81
4·58	2·63	7·21	Tr		0·08	100·04	20·21	8·75	28·96	*H*	C, Cr, Cu, Mn = Tr	3·52	82
3·57	2·05	5·62				100·33	18·88	7·85	26·73	*H*			*83
2·87	1·65	4·52				99·02	10·26	15·14	25·40	*L*		3·76	84
3·85	2·21	6·06				99·72	11·05	10·97	22·02	*L*	Sn = 0·17	3·59	85
												3·52	86
3·90	2·24	6·14		[0·06]		99·98	9·93	11·60	21·53	*L*		3·38	87
4·43	2·54	6·97		0·21	0·10	100·47	12·01	9·85	21·86	*L*			88
4·33	2·49	6·82				99·18	6·12	14·05	20·17	[*L*]			89
4·09	2·31	6·40		[0·80]		99·66	10·63	10·96	21·59	*L*		3·48	*90
3·25	1·87	5·12		0·10	—	99·96	7·27	18·91	26·18	[*L*]	C = 0·07		91
2·20	1·26	3·46		[0·16]		100·38	9·30	11·78	21·08	*L*		3·49	*92
3·43	1·97	5·40	Tr		0·04	100·28	25·22	8·76	33·98	*H*	Cr, Cu, Mn = Tr		*93
3·32	1·90	5·22				100·38	14·74	9·36	24·10	*L*		3·60	*94
3·66	2·11	5·77	0·04	[0·24]		100·07	10·70	11·63	22·33	*L*		3·51	
3·62	2·07	5·69	0·05	[0·25]		100·06	21·38	7·20	28·58	*H*		3·66	
3·64	2·09	5·73	0·05	[0·25]		100·07	15·40	9·67	25·07	All		3·58	

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consideration. Of the 192 analyses discarded, 14 are outmoded by more recent analyses given in Table 2, 22 are duplicates of other analyses in Table 1, and 48 are clearly useless because of partial or incomplete analysis, obvious extreme oxidation, impossibly low MgO statement, non-discrimination between Fe and FeO, or uncertainty of location of Fe for FeS. Thus we have actually discarded only 108 meteorites on the grounds of the criteria described above.

Table 2 gives the 94 analyses that we consider trustworthy, in alphabetical order, together with the type, density, and reference. When the author is not the analyst, the name of the analyst is given after the reference in parentheses. Unless otherwise indicated the analysis has been taken from the original reference. In these analyses, all Fe_2O_3 is calculated as FeO. NiO when listed has been

retabulated in the metal phase as Ni, and a corresponding amount of Fe in the proportion of Fe to Ni in the metallic nickel-iron has been subtracted from the FeO and added to the metallic Fe, except in the case of Daniel's Kuil where there is only enough FeO given to satisfy Cr_2O_3 and TiO_2. Chromite when given has been tabulated as FeO and Cr_2O_3. Water has been removed from the silicate phase and placed at the end of the analysis, broken down as + and − when given as such. The silicate and metal sub-totals are given, FeS is both broken down and sub-totalled as such, and the original location of the Fe for S has been found with certainty for each analysis. When given as Fe_7S_8, the troilite has been recalculated as FeS. $FeCr_2S_4$ when given has been divided into FeS and Cr_2S_3. CaS and Cr_2S_3 as well as carbon and other minor accessories are given at the end of the table, and they, as well as water, are included in the total of the analysis. Also given at the end of the table is the total iron in the metal phase, that is metallic iron plus iron in FeS, the amount of iron in the silicate phase, and the total iron in the meteorite.

Phosphorus has been tabulated as given, namely as P_2O_5 and P, though it is probable that in most cases it belongs as P_2O_5. The early analysts usually listed it as schreibersite since it was assumed that this was the only mode of occurrence of phosphorus. In all but three cases where it is listed as P it was given as such; in Chandakapur, Coon Butte, and Khetri, schreibersite was listed but the assumed composition was also given, and we have tabulated the phosphorus as P and added the iron and nickel to the metallic nickel-iron. In the analysis of Bjurbole the phosphorus was found in the silicate phase, and though listed as being in schreibersite the author states he does not know where it occurs; this phosphorus we have retabulated as P_2O_5. We have done this also for Rich Mountain, since Merrill later found phosphorus was present as merrillite [9].

Since we have recalculated the Fe_2O_3, FeO and NiO, etc., of some of these analyses, we list in Table 3 the FeO, Fe_2O_3, NiO, metallic Fe and Ni just as they appeared in the original analyses, except that chromite has been tabulated as FeO and Cr_2O_3, and iron for FeS has been taken from the correct place. In three cases Fe_3O_4 was given, as follows: Beaver Creek 0·16, Chandakapur 0·30, Rich Mountain 0·15, and this has been retabulated as FeO and Fe_2O_3. Since no other constituents but those listed in Table 3 have been altered, the original analyses of these meteorites may be obtained by simply substituting and adding the values of Table 3 into the analyses of these meteorites as given in Table 2. Asterisks before analyses in Table 2 indicate analyses whose original values must be taken from Table 3. Finally we give the average composition in Table 2; the meaning of the groups *L* and *H* will be made clear later on.

Table 4 gives the silicate phases of the chondrites in Table 2, recalculated to 100% for direct comparison with terrestrial rocks, and the average silicate phases as calculated from the average compositions in Table 2. The total iron values are also given and the analyses are arranged in order of decreasing total iron.

5. Prior's Laws and the Composition of the Chondrites

Prior [17], [18], pointed out certain regularities with respect to the distribution of iron and nickel in stone meteorites. He observed that in general if the metallic

Table 3. *Original values of* FeO, Fe_2O_3, NiO, Fe *and* Ni *before correction for Table* 2
Chondrites—superior analyses
Uncorrected constituents as given in original analyses(1)

No.	*Name*	FeO(2)	Fe_2O_3	NiO	Fe(2)	Ni	*Total* Fe(3)	*Group*
1	Albareto	14·02	2·14	0·09	4·07	0·67	20·24	*L*
3	Baroti	13·99	0·44				23·20	*L*
4	Beaver Creek	10·54	0·11	0·06	15·53	1·51	27·00	*H*
5	Benld	12·25	0·16	0·08	16·68	1·57	27·91	*H*
7	Bjurbole	13·80		0·07	6·38	0·72	20·55	*L*
8	Bowden	9·01	1·19				27·69	*H*
10	Chandakapur	20·06	0·21	0·07	5·85	0·86	24·71	*L*
12	Cobija	8·83	2·65				25·34	*H*
14	Coon Butte	13·01	2·72				21·46	*L*
15	Cronstad	9·17		0·10	16·71	1·55	27·12	*H*
17	Daniel's Kuil	0·23		0·11	23·70	1·78	29·03	[*H*]
19	Ekeby	10·82	0·07				28·71	*H*
20	Elsinora	9·14	0·17				28·49	*H*
22	Forest City	10·25		0·14	17·97	1·19	29·86	*H*
23	Forksville	19·79		0·16	5·66	0·78	23·03	*L*
30	Homestead	12·06	0·40				23·33	*L*
33	Khairpur	0·13	2·88				23·47	[*H*]
35	Kimble County(4)	17·47	0·09	0·17	10·63	0·69	26·64	*L*
36	Knyahinya	9·86	0·11				32·36	*H*
37	Lanzenkirchen	12·53	0·09				21·28	*L*
38	Launton	12·35	1·49	0·12	7·20	1·20	21·64	*L*
40	Limerick	9·94		0·19	16·81	1·51	28·10	*H*
42	Lissa	14·48	1·03				26·09	*L*
43	Lundsgard	13·62	1·50				22·58	*L*
46	Merua	7·21	0·27				27·57	*H*
49	Mezo-Madaras	15·44		0·06	8·15	1·64	24·09	*L*
51	Moorleah	14·13	0·23				21·80	*L*
52	Mount Browne	11·93	0·40				28·84	*H*
53	Narellan	13·36	3·41				25·97	*L*
61	Perpeti	11·19	4·21				22·53	*L*
64	Plantersville	12·10		0·01	16·99	1·92	28·92	*H*
67	Rangala	14·59	0·49				23·20	*L*
68	Rich Mountain	10·85	0·10				18·04	*L*
69	Rosebud	18·79		0·14	12·15	1·15	28·92	[*L*]
76	Sazovice	14·71	0·29				23·86	*L*
77	Seldebourak	11·10	3·20				29·06	*H*
80	Stalldalen	10·29		0·20	17·15	1·61	29·09	*H*
81	Strathmore	12·99	0·35				21·64	*L*
83	Tabor	10·70	0·62				28·96	*H*
90	Warbreccan	12·84	2·15	0·12	6·03	1·06	21·59	*L*
92	Wittekrantz	14·73	0·48				21·08	*L*
93	Zebrak	10·91	0·41				33·98	*H*
94	Zemaitkiemis	11·86	0·20				24·10	*L*

(1) Chromite has been divided into FeO and Cr_2O_3, and Fe_3O_4 into FeO and Fe_2O_3, when necessary.
(2) After subtraction of Fe for S when necessary.
(3) Includes Fe from FeS.
(4) Also CoO = 0·02.

Table 4. Composition of the silicate phase of superior analyses of chondrites, in order of total iron content

No.	Name	Type	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	Total	Group	Total Fe
25	Gnadenfrei	*Cc*	46·60	24·72	21·60	2·32	2·92	1·02		0·83	Tr		Tr	100·01	[*H*]	36·72
73	Saint-Sauveur	*Cek*	59·26	30·16	0·37	5·84	1·99	1·70	0·37				0·30	99·99	[*H*]	35·02
93	Zebrak	*Cc*	42·92	32·05	15·97	2·85	3·04	1·53	0·33	0·08	1·06	0·06	0·11	100·00	*H*	33·98
18	Djati-Pengilon	*Ck*	47·57	29·00	18·93	2·01	1·61	0·62	0·04	0·22	Tr			100·00	*H*	32·81
36	Knyahinya	*Cg*	43·28	32·69	13·94	3·44	4·67	0·81	0·03	0·11	0·85	0·08	0·08	99·98	*H*	32·36
32	Kernouve	*Cka*	44·04	31·65	15·64	4·26	2·53	[1·88]		Tr				100·00	*H*	31·34
2	Allegan	*Cc*	48·79	30·69	11·82	3·56	2·41	0·92	0·32	0·74	0·25	0·11	0·38	99·99	*H*	30·88
26	Gopalpur	*Cc*	50·38	26·54	16·07	3·39	2·15	0·83	0·28	Tr	0·35			99·99	*H*	30·24
22	Forest City	*Ccb*	49·38	33·19	11·24	2·88	1·97	1·12	0·08	0·14	Tr		Tr	100·00	*H*	29·86
80	Stalldalen	*Cgb*	49·32	31·98	11·19	2·91	2·22	0·86	0·21	0·55	0·35		0·41	100·00	*H*	29·09
77	Seldebourak	*Cc*	45·05	30·82	17·84	1·72	2·30	0·83	0·36	0·29	0·29	0·17	0·32	99·99	*H*	29·06
17	Daniel's Kuil	*Cek*	59·83	33·64	0·36	2·77	1·60	1·00	0·23	0·36	0·03	0·19	Tr	100·01	[*H*]	29·03
34	Khetri	*Cgb*	46·86	31·71	14·22	2·36	3·16	1·16	Tr	0·53				100·00	*H*	28·99
83	Tabor	*Ccb*	43·88	32·10	14·86	2·90	3·81	1·25	0·09	0·11	0·71	0·09	0·18	99·98	*H*	28·96
64	Plantersville	*Cia*	46·57	30·60	15·59	2·83	2·56	1·36	0·16	0·04	0·23	—	0·06	100·00	*H*	28·92
69	Rosebud	*Csa*	42·05	29·15	21·22	4·33	2·21	0·50	0·07	0·17	0·18	—	0·11	99·99	[*L*]	28·92
9	Cape Girardeau	*Cc*	46·84	31·27	14·82	2·99	1·81	1·13	0·14	0·62			0·38	100·00	*H*	28·87
52	Mount Browne	*Cc*	45·57	30·57	16·09	2·97	2·93	1·53	0·31	0·03				100·00	*H*	28·84
19	Ekeby	*Cg*	46·91	30·42	14·45	2·40	2·64	1·29	0·27	0·61	0·33	0·29	0·39	100·00	*H*	28·71
29	Hessle	*Cc*	48·14	30·34	14·21	3·11	2·35	1·23		0·07	0·55			100·00	*H*	28·53
74	Salt Lake City	*Cgb*	47·20	30·13	15·58	2·55	2·46	1·11	0·08	0·55			0·35	100·01	*H*	28·50
20	Elsinora	*Cga*	47·33	33·64	12·40	2·70	2·08	1·09	0·01	0·45	0·09	0·07	0·13	99·99	*H*	28·49
6	Benoni	*Cgb*	47·96	30·52	13·08	3·34	2·45	1·40	0·07	0·37	0·40	0·12	0·28	99·99	*H*	28·48
59	Orvinio	*Co*	50·31	30·80	10·73	3·04	3·12	1·63	0·38					100·01	*H*	28·42
40	Limerick	*Cga*	50·21	31·75	10·61	2·04	2·53	1·29	0·19	0·80	0·20		0·37	99·99	*H*	28·10
55	Oesede	*Cc*	47·94	31·32	10·77	3·65	3·99	1·78	0·54					99·99	*H*	28·04
5	Benld	*Cga*	46·40	30·45	14·81	3·66	2·46	0·97	0·26	0·13	0·40	0·13	0·35	100·02	*H*	27·91
62	Phu-Long	*Cck*	46·36	29·69	15·18	4·19	2·82	0·91	0·27	0·14	0·17		0·27	100·00	*H*	27·91
8	Bowden	*Cck*	47·78	30·24	13·25	3·79	2·90	1·00	0·14	0·42	0·32	0·16	—	100·00	*H*	27·69
46	Merua	*Cg*	49·89	31·94	10·08	3·42	2·46	0·80	0·09	0·50	0·24	0·18	0·39	99·99	*H*	27·57
58	Olmedilla de Alarcon	*Cwb*	48·20	30·80	12·26	3·29	2·82	1·14	0·25	0·50	0·34	—	0·40	100·00	*H*	27·33
15	Cronstad	*Cga*	50·01	31·70	10·82	3·24	1·95	0·90	0·09	0·50	0·05	0·40	0·34	100·00	*H*	27·12
4	Beaver Creek	*Cc*	49·48	30·46	13·02	2·48	2·11	1·06	0·16	0·55	0·27	0·09	0·33	100·01	*H*	27·00
54	Oakley	*Ck*	47·57	30·54	13·29	2·49	3·14	1·02	0·26	0·68	0·46	0·18	0·39	100·02	*H*	26·96
13	Collescipoli	*Cc*	49·63	32·01	8·12	5·02	1·61	1·79	0·33	0·82	0·42	0·25	Tr	100·00	*H*	26·88
21	Estacado	*Cka*	44·78	28·43	15·56	4·50	3·74	2·59	0·40	Tr	Tr	Tr		100·00	*H*	26·74
84	Tanezrouft	*Cg*	47·64	31·44	12·95	2·55	2·40	1·26	0·37	0·41	0·23	0·41	0·35	100·01	*H*	26·73
35	Kimble County	*Ca*	45·66	28·42	18·32	3·74	2·04	0·82	0·24	0·21	0·17	0·13	0·23	99·98	*L*	26·64
44	Mauerkirchen	*Cw*	41·36	23·56	27·87	2·72	2·46	1·08	0·52	0·42				99·99	[*L*]	26·27
91	Warrenton	*Cco*	39·07	26·44	27·31	2·45	2·43	0·77	0·26	0·65	0·22	0·17	0·22	99·99	[*L*]	26·18
42	Lissa	*Cw*	43·08	29·37	18·74	2·25	3·02	1·65	0·46	0·07	1·12	0·02	0·22	100·00	*L*	26·09
53	Narellan	*Cg*	46·86	25·73	20·02	2·68	1·90	0·73	0·29	0·54	0·59	0·16	0·50	100·00	*L*	25·97
82	Suwahib	*Cs*	49·16	27·15	12·98	5·65	2·43	1·70	0·32		0·36	0·26		100·01	*H*	25·43
85	Tieschitz	*Cc*	46·89	23·95	22·70	2·25	1·79	1·78			0·37		0·26	99·99	*L*	25·40
12	Cobija	*Ck*	47·20	29·74	14·28	3·58	3·25	0·92	0·18	0·38	0·31	0·17		100·01	*H*	25·34
31	Hvittis	*Cek*	60·08	33·61	0·49	2·24	1·07	1·82	0·46	0·22				99·99	[*H*]	24·92
10	Chandakapur	*Cib*	43·52	24·39	22·37	4·77	2·77	1·44	0·33	0·40				99·99	*L*	24·71
39	Lesves	*Cg*	46·39	26·75	18·60	3·91	1·81	1·23	0·11	1·20				100·00	*L*	24·65

94	Zemaitkiemis	*Cgb*	48·59	26·92	14·52	3·71	2·77	2·48	0·31		0·27	0·06	0·36	99·99	*L*	24·10
49	Mezo-Madaras	*Cgb*	44·03	28·84	18·06	4·08	2·01	2·11	Tr	0·65	0·22			100·00	*L*	24·09
76	Sazovice	*Cga*	45·92	27·76	17·82	3·68	2·83	[1·02]			0·83	0·07	0·06	99·99	*L*	23·86
24	Girgenti	*Cwa*	45·96	28·41	19·47	1·66	1·96	1·59		0·94	Tr			99·99	*L*	23·50
47	Meuselbach	*Ccka*	44·89	28·66	18·65	3·33	2·41	1·78	Tr	0·27				99·99	*L*	23·48
33	Khairpur	*Cek*	58·55	31·70	3·73	2·42	2·00	1·10	0·14	0·36		—	Tr	100·00	[*H*]	23·47
30	Homestead	*Cgb*	47·80	30·28	15·12	2·56	2·17	1·12	0·16	0·39	0·10		0·32	100·02	*L*	23·33
3	Baroti	*Cw*	46·93	29·25	17·04	2·84	2·12	1·08	0·05	0·21	Tr	0·19	0·30	100·01	*L*	23·20
67	Rangala	*Cwa*	46·77	28·83	17·57	2·65	2·42	0·71	0·16	0·34	0·14	0·09	0·30	99·98	*L*	23·20
23	Forksville	*Cc*	43·16	29·69	21·02	3·39	1·53	0·55	0·29	0·10	Tr		0·26	99·99	*L*	23·03
71	Saint Denis-Westrem	*Cca*	46·07	28·74	17·81	2·91	2·29	1·13	Tr	1·03	Tr			99·98	*L*	22·97
65	Prambachkirchen	*Cw*	46·05	28·05	14·89	4·64	2·68	1·39	0·28	0·06	1·45	0·14	0·38	100·01	*L*	22·87
70	Saint Christophe	*Cw*	47·03	30·97	16·33	2·57	1·81	0·61	0·22	0·47				100·01	*L*	22·78
43	Lundsgard	*Cg*	44·78	28·45	17·54	2·83	2·85	1·66	0·45	0·57	0·32	0·22	0·33	100·00	*L*	22·58
61	Perpeti	*Cw*	45·95	29·52	17·61	1·59	2·21	1·38	0·16	0·76	0·32	0·19	0·32	100·01	*L*	22·53
78	Shelburne	*Cga*	45·47	30·45	17·59	2·49	2·03	0·85	0·26	0·72	0·14			100·00	*L*	22·48
11	Chantonnay	*Cgb*	44·64	30·30	17·89	3·02	1·68	[1·36]		0·79	0·32			100·00	*L*	22·29
63	Phuoc-Binh	*Cg*	47·00	29·30	16·53	2·52	2·86	0·88	0·12		0·38		0·41	100·00	*L*	22·20
72	Saint Michel	*Cw*	46·52	28·96	15·82	3·90	1·93	1·55	0·15	0·66	0·48	0·02		99·99	*L*	22·15
86	Tourinnes-la-Grosse	*Cw*	44·09	28·71	16·61	4·29	3·07	[2·66]		0·56	Tr			99·99	*L*	22·02
45	McKinney	*Cs*	47·45	28·42	15·29	4·08	2·14	0·89	0·26	0·61	0·37	0·17	0·32	100·00	*L*	21·88
88	Varpaisjarvi	*Cw*	46·53	28·36	15·02	5·12	2·23	0·98	0·27	0·78	0·17	0·20	0·33	99·99	*L*	21·86
51	Moorleah	*C*	46·81	30·01	16·62	3·26	1·73	1·53	0·05		Tr			100·01	*L*	21·80
38	Launton	*Cia*	47·20	29·59	15·46	2·85	2·48	1·20	0·11	0·37	0·34	0·21	0·18	99·99	*L*	21·64
81	Strathmore	*Ci*	47·38	29·33	15·63	3·02	2·16	1·06	0·13	0·52	0·34	0·16	0·27	100·00	*L*	21·64
90	Warbreccan	*Cwa*	47·07	29·22	16·66	2·02	2·37	1·09	0·07	0·48	0·46	0·25	0·31	100·00	*L*	21·59
27	Grossliebenthal	*Cwa*	47·36	27·49	15·46	2·93	2·73	1·56	0·54	1·05	0·63		0·25	100·00	*L*	21·58
87	Tuan Tuc	*Cg*	46·41	28·97	17·17	3·42	2·29	0·77	0·24	0·16	0·24		0·33	100·00	*L*	21·53
14	Coon Butte	*Cib*	48·51	30·22	17·60	1·92	1·09	0·46	0·14	0·06		Tr		100·00	*L*	21·46
60	Oubari	*Cgb*	43·35	27·78	21·84	2·41	2·13	0·93	0·21	0·34	0·44	0·29	0·28	100·00	[*L*]	21·43
16	Crumlin	*Cg*	47·37	29·49	15·40	2·49	2 37	1·24	0·13	0·70	0·31	0·20	0·30	100·00	*L*	21·38
75	Saratov	*Cc*	48·01	29·37	15·23	1·94	2·65	0·59	0·11	0·77	0·42	0·13	0·80	100·02	*L*	21·36
56	Ojuelos Altos	*Ci*	48·05	30·42	13·62	3·33	2·99	0·91	0·28			—	0·41	100·01	*L*	21·28
37	Lanzenkirchen	*Cw*	46·77	27·67	14·80	5·00	1·95	2·69	0·32	0·52	0·08	0·08	0·13	100·01	*L*	21·28
92	Wittekrantz	*Cw*	46·47	28·71	17·13	2·87	2·40	1·31	0·16	0·41	0·17	0·19	0·18	100·00	*L*	21·08
48	Mezel	*Cga*	46·37	28·86	17·62	2·42	1·76	0·99	Tr	0·78	0·43	0·43	0·33	99·99	*L*	21·05
57	Olivenza	*Cc*	43·91	27·13	22·36	2·48	2·25	0·99	0·36	0·15	0·16		0·20	99·99	[*L*]	20·70
7	Bjurbole	*Cc*	47·23	29·62	15·15	2·93	2·09	1·43	0·37	0·68	0·14		0·37	100·01	*L*	20·55
1	Albareto	*Cc*	45·66	28·13	17·42	3·64	2·94	1·39	0·34	0·32	0·16	Tr		100·00	*L*	20·24
66	Rakovka	*Ci*	45·50	28·80	16·04	3·11	2·76	2·42	0·43	0·64	0·28			99·98	*L*	20·22
89	Vavilovka	"*CAm*"	44·61	28·27	20·18	1·82	2·01	1·80	0·29	0·17	0·86	—	—	100·01	[*L*]	20·17
79	Soko-Banja	*Cc*	45·79	28·31	19·59	2·34	2·12	0·94	0·08	0·40	0·06	0·11	0·27	100·01	[*L*]	20·12
41	Linum	*Cw*	55·06	32·90	1·69	3·12	4·46	1·78	0·33	0·40	0·26			100·00	[*H*]	20·09
50	Modoc	*Cwa*	50·37	30·19	14·02	2·82	1·99	0·50	Tr		0·11			100·00	*L*	18·50
68	Rich Mountain	*Cia*	48·76	31·22	12·92	3·07	2·95	0·80	0·19				0·08	99·99	*L*	18·04
28	Hendersonville	*Cc*	50·32	31·26	11·90	2·40	2·33	1·05	0·11	0·63				100·00	[*L*]	13·63
	Average:[1]															
	L Group	(53)	46·00	28·60	17·44	3·04	2·28	1·21	0·21	0·50	0·31	0·13	0·28	100·00	*L*	22 33
	H Group	(41)	48·53	30·76	12·42	3·17	2·62	1·22	0·23	0·36	0·31	0·15	0·23	100·00	*H*	28·58
	All Chondrites	(94)	47·04	29·48	15·40	3·09	2·41	1·21	0·21	0·45	0·31	0·14	0·26	100·00	All	25·07

[1] Average silicate phase of total analyses recalculated to 100%.

iron phase was low then the percent of iron in the silicates was greater and the ratio of iron to nickel in the metal phase was lower than the case in which the amount of metallic phase was large. To a rough approximation the total amount of iron is nearly constant in a large number of chondritic meteorites, and certainly much more constant than the percent of iron in the metal phase or in the silicate phases separately.

PRIOR postulated that all meteorites originated from an originally nickel poor nickel-iron magma which held the other elements in a completely reduced state. The various groups of meteorites were formed by progressive oxidation of this magma, with Si, Mg, Na, and Al oxidizing more readily than Ca and Cr which oxidize more readily than Fe. (UREY's study [21] indicates that this is not the correct order of oxidation.) Nickel would not oxidize as readily as iron and therefore becomes enriched in the residual metallic iron. Thus his classification [18], of the chondrites into groups of (1) enstatite chondrites with nearly pure magnesium silicates, high metallic iron content low in nickel, and containing CaS and Cr_2S_3, (2) bronzite-olivine chondrites, and (3) hypersthene-olivine chondrites, the latter two with increasing amounts of iron in the silicates and nickel in metallic iron, became the order of genesis according to his views. WAHL [11, p. 305] also presented data showing a progressive oxidation of the metallic constituents of certain chondrites. According to the belief of the present writers however, the initial state was highly oxidized and reduction by hydrogen and oxidation by water have produced the varying amounts of metallic iron.

Table 5. NiO *content of chondrite analyses discarded only on basis of high* NiO *content*

No.	*Name*	NiO	Fe *in Metal Phase*(1)	Fe *in Sil. Phase*(1)	*Total* Fe
3	Aguila Blanca	1·90	15·58	8·02	23·60
13	Ausson(2)	0·41	12·05	10·83	22·88
52	Ensisheim	0·46	6·69	14·03	20·72
56	Farmington	0·32	9·87	12·25	22·12
64	Gualeguaychu	0·35	19·88	9·66	29·54
91	Lake Brown	0·32	10·08	11·86	21·94
102	Malotas	0·88	18·10	7·16	25·26
104	Mangwendi	0·34	4·91	15·56	20·47
118	Morven	0·58	16·35	9·63	25·98
130	Ogi	0·30	19·10	7·02	26·12
134	Ornans(3)	2·88	5·97	19·30	25·27
141	Plainview	0·77	11·72	13·82	25·54
149	Rose City	0·47	18·03	9·32	27·35
155	Santa Isabel	1·02	8·37	13·96	22·33
162	Shytal	0·86	10·38	18·55	28·93
176	Travis County	0·52	5·02	9·27	14·29
182	Utrecht(2)	0·61	11·07	11·89	22·96
184	Waconda	0·74	9·06	12·84	21·90

(1) Values uncorrected for NiO. (2) NiO includes MnO. (3) Metallic Iron includes Ni.

In attempting to give a visual demonstration of PRIOR'S law relative to the amounts of reduced and oxidized iron, we have plotted for the chondrites the amount of iron in the combined metallic phase and troilite phase expressed as percent by weight of the entire meteorite against the amount of iron in the silicate phase, expressed in the same way. If PRIOR'S law holds then all meteorites should lie on a line making nearly 45° with each axis, the deviation being due to the necessary addition of oxygen to the whole as the axis for the completely oxidized meteorite is approached. This same law could be shown by excluding from all consideration the iron sulphide since this is present in meteorites to approximately a constant amount. Fig. 1 shows this plot for the 94 chondrites whose analyses we have selected as being trustworthy. It is evident that the distribution is discontinuous, and two separate concentrations of points are clearly prominent. For reference purposes we have called the upper group closest to the metallic iron axis the *High* group, and the lower, closest to the silicate iron axis, the *Low* group. We have roughly defined these groups by circling off the areas of prominence and have tabulated the meteorites by groups. Thus in Table 2 the letter *L* or *H* after an analysis signifies that the chondrite belongs to the low or high group in Fig. 1. Some meteorites fall out of these groups and these have been allotted for a first approximation by their position on either side of a line parallel to a 45° line from the origin and passing between the two high density regions. Those on the high group side are then marked in Table 2 with the notation [*H*] and those on the low side with [*L*]. Also in Table 2 separate averages are given for the two groups, those analyses marked [*H*] being included with the high group and those marked [*L*] with the low, and the total average for all 94 chondrites. The rare sulphides CaS and Cr_2S_3 are omitted from these averages but are included in the abundance tables drawn from these averages and presented later on. Of the 94 chondrites plotted, 53 fall in the low group and 41 in the high.

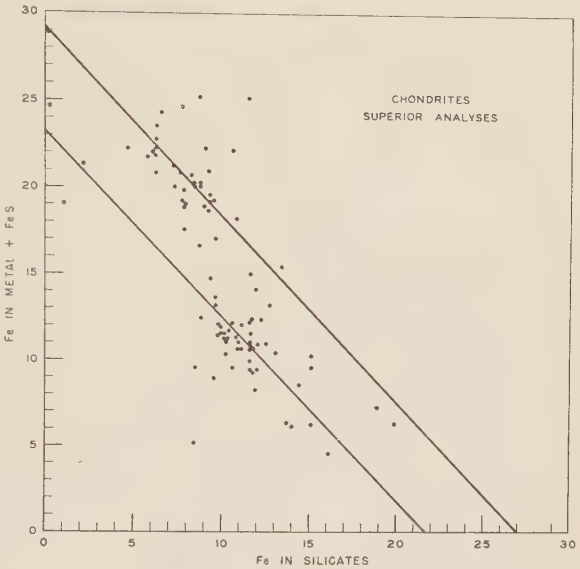

Fig. 1. Silicate phase and metal phase iron in 94 superior analyses of chondrites.

Table 5 gives the values of NiO, total iron in the metal phase (including iron from FeS), iron in the silicate phase, and total iron in the meteorite, for the 18 chondrites whose analyses were discarded only on the basis of high NiO content. It is clear that though several of these would plot off on the oxidized end of the low group, inclusion of these analyses would in no way alter the bipolar density distribution of Fig. 1. The numbers of these analyses correspond to those in

Table 1, and the iron values as listed are those originally given with no proportional redistribution for the NiO.

The diagonal lines in Fig. 1 represent lines of constant iron content (weight percent) taking into account the addition of oxygen to the mass in oxidizing

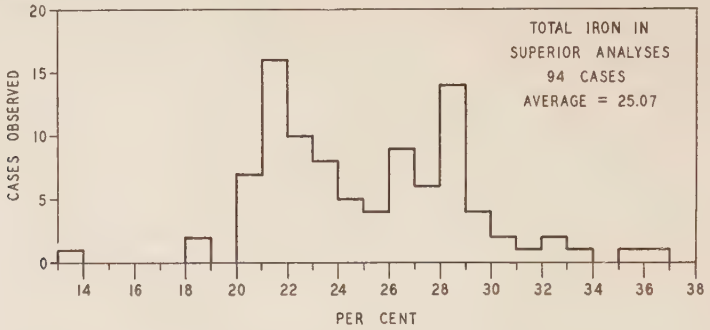

Fig. 2. Frequency distribution of total iron in 94 superior analyses of chondrites.

metallic iron. They are drawn through the points having the average amount of total iron for the two groups. Any point must move along a line parallel to these lines as portions of its iron are oxidized or reduced, and thus it is not possible to derive one group from the other by a simple oxidation or reduction process.

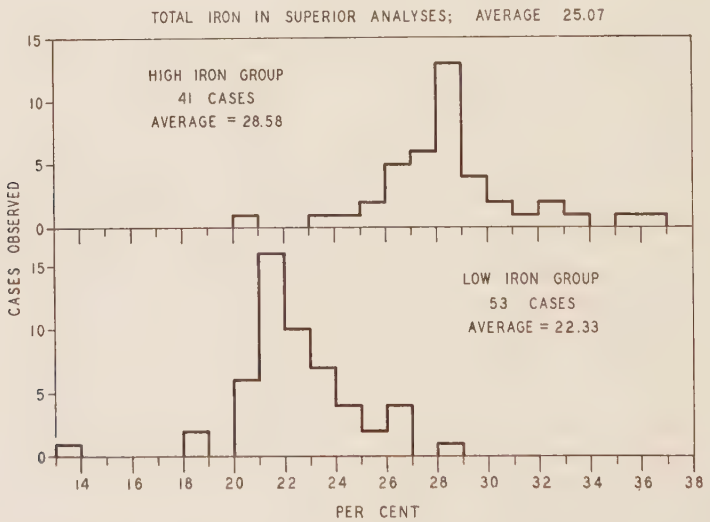

Fig. 3. Frequency distribution of total iron in low and high iron groups of chondrites.

Inspection of Fig. 1 and histograms of the frequency distribution of iron in its various phases show that the frequency distribution curve of iron in the metal phase for all chondrites possesses two maxima, while that for iron in the silicate phase possesses only one. The frequency distribution curve for total iron in all chondrites shows two maxima, which coincide with our two groups, as shown in Fig. 2, and as indicated in Fig. 1. Fig. 3 shows the histograms of total iron for the low group and high group and the small amount of overlapping

between the two groups. The overlapping may also be studied in Table 4 in which the total iron values were given along with the silicate phase compositions, the meteorites are identified as to group, and the arrangement is in order of decreasing total iron content. The distribution shown in Fig. 1 and the histograms of the groups show clearly that the two groups possess quite different amounts of total iron. Fig. 4 shows the frequency distribution of nickel in the two groups, and two maxima are again seen to be associated with the groups from Fig. 1. In Table 3 in which the original values of recalculated analyses are given, the

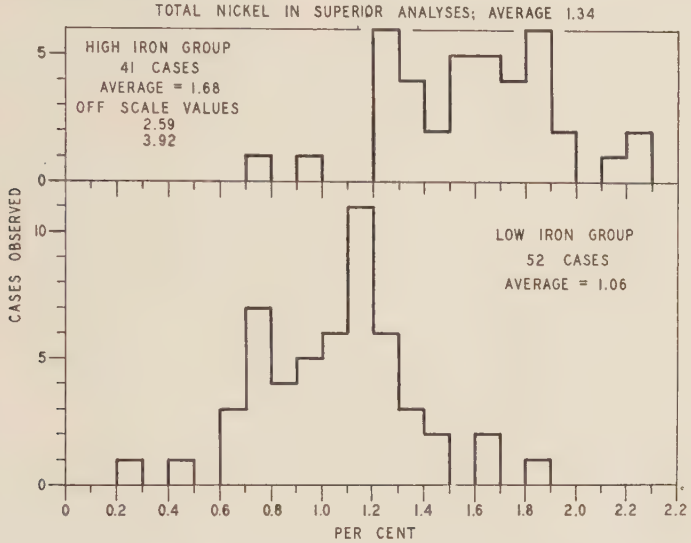

Fig. 4. Frequency distribution of nickel in low and high iron groups of chondrites.

analyses are also identified by groups and their total iron contents are given, and one may note that there is no difference in NiO distribution between the two groups, the average NiO being 0·11% in both cases.

In Fig. 5 we plot the percent of iron in the metal and sulphide phases against the percent of iron in the oxidized condition for analyses which have been discarded as unreliable. The iron for FeS has been correctly located in all the analyses plotted. It will be noted that there are indications in this plot of the two maxima which were observed much more distinctly in Fig. 1. The prominence of these two points is somewhat increased by the fact that all discarded analyses are shown in the figure and in some places these constitute duplicate analyses of the same meteorite. Reference to Table 1 will indicate the cases in which multiple analyses are shown. The general picture shown in Fig. 5 is that of a continuous scatter diagram between the points of complete reduction and complete oxidation, such as would be expected from Prior's law relative to the proportions of iron in the metallic and silicate phases. However, the lines of constant iron composition from Fig. 1 are drawn into Fig. 5, and it is clear from the distribution of points with respect to these lines in both Fig. 1 and 5 that if Prior's law and his ideas of genesis were correct, the progressive oxidation must be accompanied by a decrease

in the total iron content which is not continuous. It seems therefore, that PRIOR'S law relative to the amount of iron in the metal phase as compared with the oxide phase is only partly true, and considering the lack of precision of many of the analyses it may be largely a matter of error of analysis. In making analyses of these chondritic meteorites it is difficult to separate the iron phase from the silicate phase and sulphide phase reliably. It is done by means of magnets or chemically by the use of mercuric chloride and ammonium chloride solution in a hydrogen atmosphere which is said to dissolve only the metal phase. If any metallic iron is not removed from the silicate fraction, it would of course be classed as oxidized iron, and thus we can expect that a prominent source of error will be the failure to classify the oxidized and unoxidized iron fractions properly. Classifying metallic iron as oxidized iron moves any point on our diagrams along the approximately 45° lines to the right, and it will be noted that Fig. 5 does show clouds of points in this direction from the high concentration points indicated in Fig. 1.

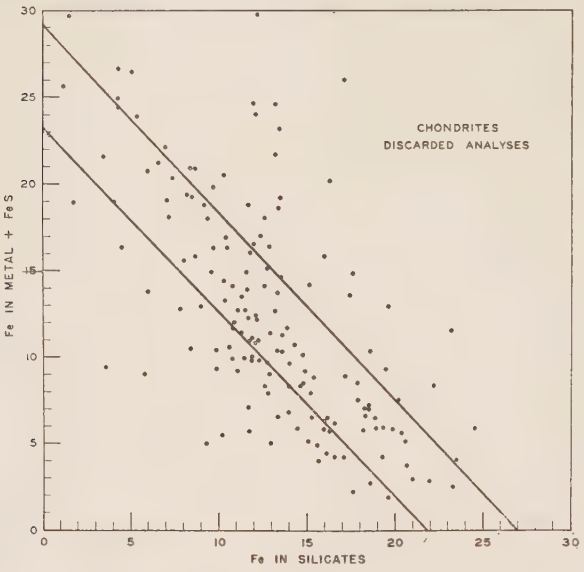

Fig. 5. Silicate phase and metal phase iron in discarded analyses of chondrites.

It appears then that there are two classes of chondrites which differ in possessing different amounts of total iron and in the relative proportions of oxidized and reduced iron. Table 6 gives the average distribution of iron between the various phases and the total iron content for the two groups. It is clear that it is not possible to form one group of chondrites from the other by oxidizing metallic iron to iron silicate or by reducing silicate phase iron to metallic iron. Moreover, it is also not possible to go from one group to the other by the addition or subtraction of metal phase, and in fact it is necessary to both oxidize or reduce iron and add or subtract iron to accomplish this transition. Thus there is no simple mixing process by which one group may be derived from the other.

Table 6 also gives the average iron nickel ratios in the metallic iron and the total meteorite for the two groups. The low group actually possesses less nickel than the high, relative to total iron, yet PRIOR'S law as stated relative to nickel holds because the amount of metallic iron in the low group becomes so much less than in the high group that the iron nickel ratio in the metallic iron of the low group cannot help but decrease from its value in the high group. This is to state, in other words, that the enrichment factor for nickel in the high group is even greater than the enrichment factor for iron, relative to the low group. We shall return to this point in a later section.

6. Other Groups among the Chondrites

Prior [18], listed the type examples for the groups in his classification as follows: (1) Enstatite chondrites—Daniel's Kuil, (2) Bronzite—olivine chondrites—Cronstad, and (3) Hypersthene—olivine chondrites—Baroti and Soko-Banja. He also listed various meteorites which fell into these groups [17], and a check of these against our tabulation shows that his bronzite-olivine group corresponds to our high group, while the hypersthene-olivine group is our low group. Since his classification is based upon the proportion of iron to nickel in the nickel-iron and MgO to FeO in the silicates this is of course not surprising, though the relationships are such that it is not at all evident that the two classifications coincide until the final results are compared. It seems to us that the Daniel's Kuil type may indeed be a very special one for the reasons which he gives as well as the definite indication that sulphides of calcium and chromium are characteristic of this group, and because the iron is nearly all in the reduced state. These types supply some of the erratic points in the higher part of our diagram in Fig. 1.

Table 6. *Average iron distribution in chondrites*

		Weight %	Fe/Ni
Low Group:			
	Fe, Metallic	7·04	6·64
	Fe in FeS	3·66	
	Fe in Metal Phase	10·70	
	Fe in Silicate Phase	11·63	
	Total Fe	22·33	21·07
High Group:			
	Fe, Metallic	17·76	10·57
	Fe in FeS	3·62	
	Fe in Metal Phase	21·38	
	Fe in Silicate Phase	7·20	
	Total Fe	28·58	17·01

On the other hand, the carbonaceous chondrites also constitute a very unusual group in that they apparently contain carbon compounds composed of carbon, hydrogen, and probably other elements, and the iron is highly oxidized. The members of this group are all "falls," which makes their oxidized condition very significant. We also find that the amphoteric chondrites occupy a rather close little group on our diagrams containing slightly less iron than our low iron group and having this iron in a somewhat more oxidized condition. We must recognize that when we have selected chondrites on the basis of analyses as described above, we may have excluded from consideration completely legitimate analyses which may be correct in every way, and it is our intention only to claim that the two groups of meteorites namely our low and high iron groups, have a real existence but not at all to exclude the possibility that other definite groups also exist.

What of course would be most satisfactory would be a complete revision of the analytical data on chondrites, as has been done to a certain degree recently by Wahl and Wiik. In this case no selection of data could then be tolerated and regularities would become evident without this procedure.

In Table 7 we list for the record the available analyses of the groups mentioned above: 7 enstatite chondrites in which, following Prior [17], we include Saint Marks (Prior suggests also that Indarch may actually belong to this group), 7 carbonaceous chondrites, and 3 amphoteric chondrites. We have classed Jelica and Vavilovka as amphoteric chondrites following the terminology of Wahl and Wiik as pointed out previously in this paper, though Wahl [20] later pointed out that these stones are actually polymict breccias containing fragments of chondrites. Moreover we have added Manbhoom to this group on the basis of von Foullon's description of the chondrules it contains (see Table 1 for reference), and have designated this group of three by the symbol "*CAm*." References for the analyses in Table 7 are not listed since they are given in Table 1 or Table 2.

Table 8 shows the distribution of the main groups of the Rose-Tschermak-Brezina system between our high and low groups of chondrites. Omitted from the table are the following: Low Group—one veined chondrite with no further distinction, one ornansite, one black chondrite, one veined black chondrite, and an amphoteric chondrite, High Group—a black chondrite and an orvinite. It is seen that the white and intermediate chondrites fall almost completely into the low group, the crystalline chondrites and enstatite chondrites lie in the high group, and the grey and spherical chondrites are evenly distributed. The chondrites designated as veined or brecciated are tabulated by totals, and the table shows that while the brecciated chondrites are evenly distributed, there are twice as many veined chondrites in the low group as in the high. A distribution study made by Brezina showed that the white and intermediate chondrites show the greatest percent of veined members [19, p. 85], and since these fall into the low group the predominance of veined chondrites in the low group is explained.

Table 8 also shows the distribution of those chondrites in which the original reference describes the frequency of chondrules as "few" or "abundant" or equivalent terms. The table shows that while chondrites with many chondrules are evenly distributed between the low and high groups, those chondrites in which chondrules are scarce tend to fall mainly in the low group. It is generally known that the white chondrites and the enstatite chondrites are characterized by their scarcity of chondrules. Thus if we break down those meteorites with few chondrules by classes we find the following distribution. In the low group are found 7 white chondrites, 2 intermediate chondrites, 3 grey chondrites, 1 chondrite unclassified, and 1 amphoteric chondrite, total 14. In the high group are found 3 enstatite chondrites, 1 grey chondrite, and 1 crystalline chondrite, total 5. In the chondrites listed as possessing many chondrules, those in the low group are 3 white chondrites, 1 intermediate chondrite, 6 grey chondrites, 7 spherical chondrites, 1 veined crystalline spherical chondrite, 1 veined chondrite further unclassified, and 1 veined black chondrite. In the high group are 9 spherical chondrites, 6 grey chondrites, 2 crystalline chondrites, 1 intermediate chondrite, and 1 black chondrite. Thus it is clear that the large number of low group chondrites

Table 7. Analyses of special groups of Chondrites

Name	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	Fe	Ni	Co	Fe	S	FeS	C	H_2O+	H_2O-	*Total*	*Accessories*
I AMPHOTERIC CHONDRITES																						
Jelica	39·72	25·34	21·34	1·88	1·23	[0·12]		0·68	0·21			1·61	0·83	0·05	4·50	2·59	7·09				100·10	Cu = Tr
Manbhoom[1]	40·12	27·30	19·86	1·80	1·93	0·44	0·20	0·55	0·07			2·38	0·91		2·96	1·70	4·66				100·42	P = 0·20
Vavilovka	39·96	25·32	18·08	1·63	1·80	1·61	0·26	0·15	0·77	—	—	1·79	0·93	0·06	4·33	2·49	6·82				99·18	
II CARBONACEOUS CHONDRITES																						
Cold Bokkeveld[2]	30·80	22·20	29·94	2·05	1·70	[1·23]		0·76	0·97		Tr	2·50	1·30	Tr		3·38	9·27	1·67			98·78	Cu = 0·03, "bitumen" = 0·25
Felix	33·57	19·74	26·22	3·24	5·45	0·62	0·14	0·80	0·68			2·59	0·36	0·08	3·02	1·74	4·76	0·36	[0·16]		99·79	Cu = 0·01, NiO + CoO = 1·01
Indarch	35·70	16·92	14·94	1·97	0·70				0·13		0·52	10·40	0·95	0·02	8·43	4·84	13·27	0·31	[2·80]		100·31	CaS = 0·60, CO_2 = 0·27, NiO = 0·55, CoO = 0·05, Mn = 0·12, P = 0·09
Kaba	34·24	22·39	26·49	5·38	0·66	[0·30]		0·60	0·05			2·88	1·37	Tr	2·25	1·30	3·55	0·58			98·50	Cu = 0·01
Nogoya[3]	27·18	19·05	20·28	2·35	2·52	[0·18]		0·35	0·07				[1·61]		5·70	3·27	8·97				97·35	Heat Loss = 14·79, Cu, Sn = Tr
Orgueil[4]	26·08	17·00	22·93	0·90	1·85	2·26	0·19	0·33	0·36						8·53	4·90	13·43				99·22	H_2O + Organic Matter = 13·89
Staroye Boriskino[5]	26·73	19·35	24·52	3·11	2·22	1·07	0·20	0·30	0·15	0·15			1·15	0·03	1·78	1·02	2·80	3·75	8·72	2·96	97·21	
III ENSTATITE CHONDRITES																						
Blithfield[6]	42·22	24·64	2·10	2·08	0·87	0·92	0·09		0·15	0·07	0·04	11·71	1·10	0·08	7·37	4·23	11·60	0·16	1·10	0·19	99·70	Cr_2S_3 = 0·46, Cu = 0·01, CuO = 0·07, P = 0·04
Daniel's Kuil[7]	38·47	21·63	0·23	1·78	1·03	0·64	0·15	0·23	0·02	0·12	Tr	23·70	1·87	0·12	5·15	2·94	8·09	0·32	[0·34]		99·89	CaS = 0·86, Cr_2S_3 = 0·29
Hvittis	41·53	23·23	0·34	1·55	0·74	1·26	0·32	0·15				20·04	1·96	0·07	4·62	2·65	7·27				99·96	CaS = 0·86, Cr_2S_3 = 0·56, P = 0·08
Khairpur[8]	42·64	23·09	2·72	1·76	1·46	0·80	0·10	0·26		—	Tr	16·83	1·29	0·17	4·53	2·59	7·12	0·41	[0·20]		99·39	CaS = 0·34, Cr_2S_3 = 0·20
Pillistfer	38·59	23·67	1·52	2·51	0·48	0·34	0·24	0·49	0·02			19·59	1·88	Tr	6·08	3·49	9·57				98·91	P = 0·01
Saint Mark's	38·29	18·23	6·50	0·64	1·08	0·85	0·23		0·33			17·66	1·84	0·21	8·78	5·04	13·82	0·36			101·15	CaS = 0·50, Cl = 0·27, Mn = 0·29, P = 0·05
Saint-Sauveur	33·40	17·00	0·21	3·29	1·12	0·96	0·21				0·17	25·73	1·62	0·12	9·13	5·24	14·37	0·10	[0·09]		99·74	CaS = 1·15, Cr_2S_3 = 0·15, Mn = 0·05

[1] 0·83 Fe_2O_3 recalculated as FeO. Author found 0·42 Ni in silicate phase which he added to metal phase. We have transferred a proportional amount of iron = 1·10%.
[2] Author gives S combined with metal phase as NiS + Fe_2S_3.
[3] All iron was given as Fe_2O_3. Combustion in oxygen stream yielded C = 1·56, H_2O - 14·03. Drying at 110°C yielded H_2O = 3·43%.
[4] Analysis No. 133 in Table 1. 7·78 Fe_2O_3 was recalculated as FeO.
[5] All iron was given as Fe_2O_3. Carbon includes CO_2.
[6] 2·46 Fe_2O_3 recalculated as FeO and 0·12 SO_3 as FeS. NiO = 0·26 and CoO = 0·03 were recalculated as Ni and Co.
[7] 0·11 NiO recalculated as Ni.
[8] 2·88 Fe_2O_3 recalculated as FeO.

with few chondrules is dependent on the fact that there are so many white chondrites and that the white chondrites tend in the main to have few chondrules.

Wahl [20] has pointed out that the brecciated chondrites tend to be "polymict," that is they enclose fragments of a foreign material as compared with the surrounding principal mass of the stones. He has studied some of the chondrites and described the fragments they contain with reference to their type according to the Rose-Tschermak-Brezina classification. We find that of the chondrites in our tabulation of trustworthy analyses which Wahl has described, seven polymict breccias fall into our low group and only three in the high group, but the total is too small to attach any significance to the distribution.

Table 8. Distribution of Rose-Tschermak-Brezina classes between high and low group chondrites

Type	*Low Group*	*High Group*	*Total*
Cw	11	1	12
Cwa	5	0	5
Cwb	0	1	1
Ci	3	0	3
Cia	2	1	3
Cib	2	0	2
Cg	6	4	10
Cga	3	4	7
Cgb	5	4	9
Cc	9	10	19
Cca	1	0	1
Ccb	0	2	2
Cck	0	2	2
Ccka	1	0	1
Ck	0	3	3
Cka	0	2	2
Cek	0	4	4
All Veined	14	7	21
All Brecciated	7	6	13
Few Chondrules	14	5	19
Many Chondrules	20	19	39

If the division of the chondrites into our low and high groups has some genetic significance, as we believe it does, it is possible to postulate that if any types of chondrites occur predominantly in one of our two main groups, then types that fall mainly in the low group should not include fragments of types that fall mainly in the high group and vice-versa. In the chondrites studied by Wahl there are

a few cases to which such criteria may be applied. WAHL'S results show that the intermediate chondrites contain fragments of rodites, amphoterites, diogenites (another name for chladnites), and white chondrites. Since the intermediate chondrites and white chondrites occur mainly in our low group, we might expect the rodites, amphoterites, and diogenites to be closely allied to the low group. We have already seen that the amphoteric chondrites all occur in our low group. The following specific instances given by WAHL can be checked with the information we have.

1. Bettrechies *Cg*, contains *Cw* and *Am* fragments and thus should be in our low group. The analysis was discarded for $Al_2O_3 = 0{\cdot}18$, but it has 14·64% metal phase iron and 13·55% silicate phase iron and thus plots in our low group even though the total iron content is equal to the average for the high iron group.

2. Oubari *Cg*, contains *Ci* and *Am* fragments and thus should be a member of the low group, as it is.

3. Farmington *Cs*, contains *Am* fragments and thus should be low. The analysis was discarded for $NiO = 0{\cdot}32$, but it has 9·87% metal phase iron and 12·25% silicate phase iron and thus plots in the low group.

4. Plainview *Cck*, contains rodite fragments and should be in the low group. The analysis was discarded for $NiO = 0{\cdot}77$, but metal phase iron is 11·72% and silicate phase iron is 13·82% so that it plots in the low group, but would not if corrected for the large amount of nickel-oxide, assuming the validity of so large a correction.

5. Hedjaz *Cg*, contains diogenite fragments and should be in the low group. The analysis was discarded for $K_2O > Na_2O$, but it has 12·98% metal phase iron and 8·94% silicate phase iron and does indeed plot in the low group.

6. Soko-Banja *Cc*, contains diogenite fragments, should plot in the low group, and does.

7. Shelburne *Cga*, contains diogenite fragments, should plot in the low group, and does.

8. Ochansk *Cca*, is described as containing a microcrystalline basic fragment too fine grained to determine accurately but which may correspond to an amphoterite. MERRILL'S discarded analysis (for $Al_2O_3 = 7{\cdot}11$, $NiO = 0{\cdot}56$) gives 19·41% metal phase iron and 8·18% silicate iron and it thus plots in the high group, rather than in the low, as would be expected if the fragment is an amphoterite.

9. Parnallee *Cga*, contains *Cw* and chladnite fragments and should thus plot in the low group. The analysis was discarded for $CaO = 0{\cdot}56$, $NiO = 0{\cdot}72$, $Na_2O = 1{\cdot}91$, but it gives metal phase iron 9·83%, silicate phase iron 11·87%, and thus plots in the low group.

It is unfortunate that more analyses and determinations of fragments do not exist for the same stones, and that checks are available for only the low group. It is hoped that more studies of this type will be made; it would be particularly interesting if included fragments of enstatite chondrites and crystalline chondrites, both of which are characteristic of our high group, were found in such studies. At any rate, the consistency of all possible checks with the exception of two doubtful cases (cases 1 and 8) indicates the strong possibility that the polymict

breccias were constructed within the two groups we have established rather than in any sort of mixing process between the two groups.

7. COMPOSITION OF THE ACHONDRITES

PRIOR [17], [18] divided the achondrites into two main groups: calcium poor achondrites in which feldspar is generally oligoclase, and calcium rich achondrites in which feldspar is generally anorthite. We have called these groups respectively the chondritic type and the basaltic type achondrites in order to emphasize the division between the two groups and their general similarity to two familiar groups of well-known chemical composition.

Table 9 gives the available analyses of the chondritic type achondrites. The analyses are few and in many cases quite old so it is difficult to be sure of anything but the general amounts of the major elements. We have not listed two analyses which appear to be quite incorrect. WEBSTER'S old analysis of Nobleborough [27], made in 1824, gives 15% of total iron all as metallic iron, and 18% sulphur, with about 5% alumina and no calcium or alkalis; almost certainly an impossible composition. MASKELYNE'S analysis of Shalka [28] shows almost 18% chromite and thus is probably not a representative sample since the other analyses of Shalka show quite normal amounts. We have also not listed VON HAUER'S analysis of Shalka [29] which was made on selected material rather than a total sample, and J. L. SMITH'S analysis of Bishopville [30] which was made only on the enstatite of the meteorite (i.e. he was proving the material was enstatite).

Several analyses are duplicated in Table 9 since they differ somewhat, though the differences are not great except in the case of Bustee where number 4, by DANCER, is probably more representative since MASKELYNE'S analysis was made

Table 9. Analyses of

No.	*Name*	*Type*	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	*Silicate*	Fe	Ni
1	Bishopville[1]	*Bu*	57·03	33·51	1·27	1·71	1·50	1·03	0·09		0·19			96·87	0·18	0·04
2	Bishopville[2]	*Bu*	57·52	34·80	1·12	2·72	0·66	1·14	0·70		0·20			98·86		
3	Bustee[3]	*Bu*	52·87	28·32	1·08	—	12·40	0·57	0·24					95·48		
4	Bustee	*Bu*	52·73	37·22	4·28	—	1·18	—	Tr		0·01		Tr	96·20		
5	Ellemeet	*Ro*	53·63	25·65	18·01					1·82	1·35			100·46		
6	Goalpara	*U*	40·36	37·45	13·32		0·60							91·73	8·49	
7	Ibbenbuhren[4]	*Chl*	54·49	26·27	17·34	1·16	1·21				0·28			100·75		
8	Johnstown[5]	*Chl*	49·83	26·62	13·64	2·33	2·61	0·33	0·10	1·00	0·40		0·03	96·89	0·84	0·03
9	Manegaon	*Chl*	55·63	23·32	20·81		1·49			0·70				101·95	Tr	
10	Pena Blanca Spring	*Bu*	57·70	37·96	1·99	0·21	1·08					0·06		99·00	0·48	0·02
11	Roda	*Ro*	50·38	27·10	14·91	2·86	1·42	0·38	0·31	0·64	0·22		0·04	98·26		
12	Shalka	*Chl*	52·51	28·35	16·81	0·66	0·89	0·22		1·25				100·69		
13	Shalka	*Chl*	51·85	27·14	18·96		0·08	0·80		1·64				100·47		
14	Shallowater	*Bu*	51·44	34·74	0·70	0·25	0·47	0·21	0·04	0·05			0·44	88·34	7·97	0·60
15	Tataouine	*Chl*	54·94	27·42	14·35	0·62	0·76			0·35	0·26	0·19	—	98·89	0·79	
	Average[6]		52·56	30·47	11·45	1·09	1·20	0·36	0·11	0·83	0·39	0·12	0·10	98·68	2·68	0·17
16	Norton County[7]	*Bu*	56·61	39·34	0·60	0·71	1·66	0·10	0·26	0·12	0·38	0·06	0·07	100·18	91·16	5·82

[1] 1·41 Fe_2O_3 recalculated to FeO. FeS observed but not present in portion analyzed.

[2] 1·25 Fe_2O_3 recalculated to FeO.

[3] Fe, Ni, FeS, Fe_3P, and $FeCr_2O_4$ observed but not included in analysis.

[4] Average of analyses of pyroxene crystals and ground mass.

[5] 0·86 SO_3 recalculated as FeS.

[6] Numbers 2, 3, and 13 omitted from average.

[7] Proportion of silicate to metal phase not given. Silicate phase includes accessories and NiO = 0·04, CoO = 0·005. Metal phase includes SiO_2 = 0·07, Al = 1·00, P = 0·015, Cr = 0·061, and Cu = 1·20.

from selected material occurring around a nodule of CaS. We have included only what appears to be the better of each set of duplicate analyses in the average. As in the case of the chondrites, FeS has been assigned correctly and chromite divided into FeO and Cr_2O_3, but no other changes in the analytical statements have been made. The analytical statements of Johnstown, Pena Blanca Spring, Shalka (by RAMMELSBERG), and Shallowater were given in such a fashion that recalculation to the bulk composition of the stone is rather uncertain, and in the case of Norton County this recalculation cannot be made for the necessary information is not given by the authors.

The average composition of the chondritic type achondrites is rather like that of the chondrites, except of course that they contain much less metal phase and iron sulphide than the chondrites. However, this is only a general similarity, since comparison of this average with the silicate phase composition of the chondrites given in Table 4 shows that they actually contain somewhat more silica and magnesia, and lesser amounts of ferrous oxide, alumina, lime, and alkalis, than do the chondrites. There are actually two main groups of these chondritic type achondrites, the bustites and chladnites. Bishopville, though generally listed as a chladnite, is actually a bustite as shown by its chemical composition. (PRIOR [17, p. 37] has discussed the confusion resulting from the fact that the term "chladnite" was originally applied to Bishopville.) We have also included Norton County as a bustite, since the slight differences in its composition from that of the bustites do not justify the introduction of a new type into an already confused classification. These bustites* contain nearly pure enstatite, small

* Aubres is a typical chladnite as shown by WAHL [20]; therefore the name bustites rather than aubrites should be used for this group.

chondritic type achondrites

Co	*Metal*	Fe	S	FeS	H_2O	*Total*	*Total* Fe	*Accessories*	*Sp. Gr.*
	0·22				1·99	99·75	1·17	NiO = 0·54, CoO = Tr, CaS = 0·67	
						99·66	0·87	Loss 0·80	
						100·07	0·84	CaS = 4·13, $CaSO_4$ = 0·44, Li_2O = 0·02	
					0·92	99·47	3·33	NiO = 0·78, $CaCl_2$ = 0·01, $CaSO_4$ = 1·58, Na_2S = 0·76, Li_2O = Tr	
		0·73	0·42	1·15		101·61	14·72		
	8·49		Tr			101·07	18·84	C = 0·72, H = 0·13	
						100·75	13·47		3·41
Tr	0·87	0·98	0·57	1·55		99·31	12·42	P = Tr	3·41
						101·95	16·17		3·20
Tr	0·50	0·79	0·46	1·25		100·75	2·82	Mn = Tr	
		1·10	0·63	1·73	0·50	100·49	12·69		
		0·25	0·14	0·39		101·08	13·31	P = Tr	
						100·47	14·73		
	8·57	0·78	0·45	1·23		98·14	9·29		
	0·79	0·22	0·13	0·35	0·14	100·17	12·16		3·40
Tr	2·85	0·61	0·35	0·96	0·89	103·38	12·19		3·35
0·37	99·70	-			0·10			Cl = 0·08, CuO = 0·033, MoO_3 = 0·003, PbO = 0·008, SnO_2 = 0·001	

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Table 10. *Analyses of*

No.	*Name*	*Type*	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	*Silicate*
1	Angra dos Reis	*A*	43·94	10·05	8·56	8·73	24·51	0·26	0·19	Tr		2·39	0·13	98·76
2	Atsuma-Mura[2]	?	47·84	8·49	2·54	24·34	13·40	1·52	0·21		0·17		0·32	98·83
3	Bereba	*Eu*	48·48	6·50	18·76	12·25	11·12	0·15	0·22	0·88	0·25	0·60	0·12	99·33
4	Binda	*Eu*	50·50	16·15	15·29	8·84	6·15	0·28	0·13	0·75	0·51		0·03	98·63
5	Cachari[3]	*Eu*	48·47	6·84	19·98	13·94	8·62	0·92	0·13	0·06	0·78	0·07	0·06	99·87
6	Frankfort	*Ho*	51·33	17·59	13·19	8·05	7·03	0·45	0·22	0·42				98·28
7	Jonzac	*Eu*	48·32	7·42	17·76	12·73	10·48	0·91	0·22	0·33	0·28	0·52	0·16	99·13
8	Juvinas	*Eu*	49·02	6·80	17·56	13·39	10·72	0·40	0·17	0·31	0·21	0·58	0·17	99·33
9	Le Teilleul	*Ho*	48·14	13·93	16·71	11·35	7·88	0·22	0·24	0·53	0·22	0·19	0·17	99·58
10	Luotolax[4]	*Ho*	48·05	8·67	18·56	13·41	10·40	[0·29]		0·60	0·25			100·68
11	Lyubimovka	*Eu*	49·45	17·40	15·61	9·66	6·39	[0·31]		0·04	0·72		0·01	99·59
12	Macibini	*Eu*	49·10	8·43	15·99	11·71	10·31	0·62	0·06	0·42	0·51	0·74	0·09	97·98
13	Massing	*Ho*	53·11	8·48	18·99	8·20	5·79	1·93	1·19	0·98				98·67
14	Moore County	*Eu*	48·16	8·41	15·02	15·57	11·08	0·45	0·09	0·44	0·31	0·32		99·85
15	Nakhla	*A*	48·96	12·01	20·66	1·74	15·17	0·41	0·14	0·33	0·09	0·38		99·89
16	Padvar-ninkai[5]	*She*	47·21	9·00	16·17	10·49	12·18	1·20	0·86					97·11
17	Pasamonte	*Eu*	48·20	6·47	17·04	13·91	10·24	0·31	0·06	0·30	0·42	0·07	—	97·02
18	Pavlovka	*Ho*	50·91	14·69	17·42	6·30	6·24	2·04	0·43		0·30	0·03		98·36
19	Peramiho	*Eu*	49·32	7·15	19·99	11·24	10·84	0·40	0·25			0·42		99·61
20	Petersburg[5]	*Ho*	49·21	8·13	20·41	11·05	9·01	0·82	—				Tr	98·63
21	Serra de Magé	*Eu*	43·42	3·18	6·56	27·20	14·53	1·59	0·20	0·33	0·58	—	—	97·59
22	Sherghotty	*She*	50·21	10·00	21·85	5·90	10·41	1·28	0·57		Tr			100·22
23	Stannern	*Eu*	47·94	7·14	20·05	11·19	10·36	0·75	0·13	0·35		0·41	0·14	98·71
24	Tchervony Koot	*Eu*	48·80	6·98	18·47	13·44	11·48	0·52	0·12	0·21	0·63	0·71		101·36
25	Zmenj	*Ho*	48·18	16·81	14·66	8·06	5·48	1·75	0·38	0·38	2·17		0·08	97·95
	Average		48·65	9·87	16·31	11·71	10·39	0·83	0·27	0·40	0·47	0·50	0·10	99·50

(1) Fe_2O_3 as given in analytical statement. Recalculated as FeO here.
(2) 0·50 SO_3 recalculated as FeS.
(3) 0·06 SO_3 recalculated as FeS.
(4) Average of analyses of (1) black crystals, (2) ground mass.
(5) Location of Fe for S not given.
(6) Fe_2O_3 from No. 18 omitted.

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amounts of ferrous oxide, and in some cases calcium sulphide; thus except for the small content of nickel-iron and iron sulphide and the lack of chondrules, they are similar to the enstatite chondrites of which Daniel's Kuil is the type example.

The other main group of these achondrites is that of the chladnites*. These stones consist mainly of hypersthene, and are similar to our low iron group of chondrites with respect to magnesia and ferrous oxide, though the silica content is greater and they have smaller amounts of lime, alumina and alkalis.

* This name has now become associated with the types also known as diogenites (*vide supra*), but we prefer to retain the name chladnite in honour of Chladni.

Basaltic Type Achondrites

Fe	Ni	*Metal*	Fe	S	FeS	H_2O+	H_2O-	*Total*	*Total* Fe	Fe_2O_3[1]	*Accessories*	*Sp. Gr.*
			0·81	0·45	1·26			100·02	7·46	0·31		
			0·35	0·20	0·55	[0·33]		99·71	2·32	0·71		2·87
			0·36	0·21	0·57	0·15	0·18	100·23	14·94	0·30		
0·45		0·45	0·61	0·35	0·96		0·10	100·22	12·94		C = 0·07, CuO = Tr, V_2O_3 = 0·01	3·25
			0·03	0·02	0·05	[0·20]		100·12	15·55	0·24	NiO = Tr	3·13
Tr	Tr		0·40	0·23	0·63			98·91	10·65			3·31
			0·19	0·11	0·30	0·35	0·05	99·83	13·99	0·19		3·18
Tr			0·17	0·10	0·27	0·14	0·30	100·04	13·81	0·44		3·12
			0·17	0·10	0·27	0·16	0·06	100·07	13·15	2·35		
								100·68	14·42		SnO_2 = 0·45	
			0·31	0·18	0·49			100·08	12·44	2·88		3·30
1·58	Tr	1·58	0·37	0·21	0·58	0·13		100·31	14·37	—	C = 0·04	3·00
	Tr		0·64	0·37	1·01			99·68	15·40			
			0·52	0·30	0·82			100·67	12·19	1·90		
			0·10	0·06	0·16	0·17	0·07	100·29	16·15	1·29		
1·56				0·51	1·40			99·61	14·12	2·70	C = 0·43, Mn = Tr	
[2·64]		2·64	0·12	0·07	0·19			99·85	16·00	0·79		
0·10						[0·44]		99·02	13·54	12·74	Cu = 0·12	3·33
			0·51	0·29	0·80			100·41	16·04	—		3·08
0·50	Tr			0·06	0·16			99·23	16·36		Mn = 0·04	3·20
			0·07	0·04	0·11	1·71	0·01	99·42	5·17	2·07		2·95
Tr				Tr				100·22	16·98	3·15		3·28
Tr			0·55	0·31	0·86	0·30		99·87	16·13	1·20	NiO = 0·25, Co = Tr	3·05
			0·16	0·09	0·25			101·61	14·51	—		3·15
0·21	0·11	0·32	0·84	0·48	1·32			99·59	12·44			
			0·36	0·21	0·57	[0·40]		100·47	13·24	1·14[6]		3·15

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The amphoterites are discussed above; the rodites are apparently quite similar though somewhat more brecciated. The ureilites contains crystals of olivine and pyroxene enclosed in a mesh of nickel-iron and carbonaceous matter, and thus appear to be somewhat related to the stony irons except for the low metal content.

In general, this group of achondrites resembles chondrites in which chondrules have been destroyed and the metal and sulphide phases separated from the mass, perhaps during a melting process caused by a close approach to the sun or by some slightly higher temperature during the formation of the chondrites. If high accelerations were present, either due to gravitational fields or to kinetic acceleration, iron could be separated from silicate, and if the heating process was not too

Table 11. *Discarded analyses of basaltic type achondrites*

No.	*Name*	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	K_2O	Cr_2O_3	MnO	TiO_2	P_2O_5	Fe	Ni	Fe	S	*Total*	*Accessories*
1	Calivo[1]	38·53	1·20	7·11	15·57	10·32	0·73	0·25		0·35		0·16	19·03			2·83	99·83	Cl = 1·69, NiO = 2·06
2	Constantinople	48·59	6·16	21·13	12·63	10·39	0·46	0·16	0·30	Tr						Tr	99·82	
3	Jonzac	49·70	6·86	20·29	11·80	10·36	0·50	0·14			Tr						99·97	H_2O = 0·32
4	Juvinas[2]	49·23	6·44	21·42	12·55	10·23	0·63	0·12	0·24		0·10	0·28			0·16	0·09	101·49	
5	Juvinas[3]	47·99	7·20	18·70	13·50	10·60	0·55	—	Tr		0·57	—	Tr		0·10	0·06	99·38	NiO = 0·11, CoO = Tr
6	Nakhla	49·98	12·20	19·58	1·65	15·12	Tr	Tr	0·23	Tr	Tr						99·11	H_2O = 0·35, V_2O_3 = Tr
7	Padvarninkai[4]	46·78	6·78	19·77	12·05	10·86	2·11	1·97									100·32	
8	Pampa del Infierno[5]	38·86	20·05	13·06	11·95	2·70	0·57	0·07	0·63	0·62	—	0·33	2·92	0·39	5·28	3·03	100·58	Co — 0·08, P = 0·01, SnO_2 — 0·03
9	Stannern	48·30	6·87	19·49	12·65	11·27	0·62	0·23	0·37	0·81						Tr	100·61	

[1] Location of Fe for S not given.
[2] 1·21 Fe_2O_3 recalculated to FeO.
[3] 0·22 Fe_2O_3 recalculated to FeO.
[4] 3·81 Fe_2O_3 recalculated to FeO.
[5] 0·10 Fe_2O_3 recalculated to FeO. Also NiO and CoO = Tr.

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prolonged or too violent no great change in chemical composition would result. It is interesting that in a recent investigation [31] AHRENS, PINSON, and KEARNS have shown that Johnstown, a chladnite, has very small amounts of potassium and rubidium. Since the alkalis are the most volatile constituents of the silicate phase, these data suggest a heating process of some sort.

Table 10 gives the analyses of the achondrites which we have termed the basaltic type. In this group we have more and generally better analyses than in the case of the chondritic type achondrites; those of LACROIX and his co-workers appear to be quite carefully done. Thus we have not included the duplicate analyses of Jonzac, Juvinas, Nakhla, Padvarninkai, and Stannern, which agree almost perfectly with those included in Table 10 except for Padvarninkai, and in these cases Table 10 gives the analysis which we believe to be better. The unused duplicate analyses are given for comparison in Table 11. Also we have not used the analyses of Constantinople by LUDWIG, and Sherghotty by CROOK. Constantinople is chemically and mineralogically identical with Stannern and TSCHERMAK states that most probably this is a sample of Stannern given a different name by a mixup in catalogues. (See Constantinople reference in Table 11.) CROOK'S analysis of Sherghotty differs greatly from that of LUMPE and TSCHERMAK has checked the analyses and shown that CROOK must have analyzed the wrong sample. (See Sherghotty reference in Table 10.) Two analyses have been discarded on suspicion of being incorrect and are also listed in Table 11. Pampa del Infierno has the highest amount of iron, magnesium, and iron sulphide, and the lowest amount of calcium, of all the basaltic achondrites, and does not agree at all with any other representative of this group. Calivo has 19% metallic iron only 1% magnesia, and almost 3% sulphur; the analysis appears to be incorrect.

These basaltic type achondrites correspond to PRIOR'S calcium rich achondrites in which the feldspar when present is generally anorthite. The angrites differ markedly from the others in their high calcium content; Angra dos Reis is composed almost entirely of augite, while Nakhla is composed of calcium rich hedenbergite-diopside and iron rich olivine. The eucrites and howardites include two somewhat different general groups, one of which corresponds rather closely to terrestrial oceanites, the other to olivine basalts and more specifically to the Disko Island basalt with regard to the high ferrous oxide content. We do not wish to present a detailed discussion of the composition of the achondrites in this paper, but it should be pointed out that since the substantial percentage of nickel in the metal phase of the Disko basalt seems to indicate a deep seated origin, there is thus some evidence that the mantle of the earth may consist of material of the same primordial composition as that which produced the basaltic type achondrites. Furthermore, the general similarity of this second group of achondrites to terrestrial basalts is strong indication that melting and differentiation processes have played an important part in their formation. The structure of these basaltic achondrites is generally quite similar to the ophitic and gabbroic textures observed in basic terrestrial rocks; quite different from the tuffitic features observed in the chondrites. The eucrites are composed mainly of calcium rich clino-hypersthene (or hedenbergite-hypersthene) and anorthite; Sherghotty differs mainly by possessing glassy rather than crystalline feldspar. The howardites generally

contain hypersthene, clino-hypersthene, and anorthite, and are characterized by a brecciated structure, often containing fragments of eucrites; they are thus polymict breccias as discussed by Wahl [20].

In summary, one sees that the achondrites generally appear to have undergone partial or perhaps complete fusion as evidenced by their structure and composition. One type possesses a composition similar to that of terrestrial basalts and it would thus seem that fractional crystallization or fractional melting processes have played at least an important part in their formation as has been pointed out previously by others. The other type however is similar to the chondrites in general composition and thus it appears that some process such as volatilization during reheating perhaps accompanied by a small amount of crystal fractionation has been the factor which produced the small differences from the composition of the chondrites.

8. The Origin of Meteorites

Before undertaking a discussion of the abundances of the elements as derived from these analyses of meteorites, it is desirable to try to envision some possible cosmic process by which the meteorites may have been produced. A glance at a chondrite will convince an observing student of this subject that the process by which it was formed cannot possibly have been a simple one. The great variation in mineralogical composition, colour, polymict character as described by Wahl, cracks and fissures filled with veins of various minerals, particularly iron, the imbedding of chondrules of nearly pure minerals in many cases in a ground mass of complex composition, and the presence of glass in the chondrules and in the matrix, make it certain that a very complex process or processes were responsible for the formation of these objects. The absence of water-containing minerals such as the micas and hornblendes indicates that they were not formed under the conditions obtaining within a planet of large size. It can be stated certainly that after they were finally put together they were never heated to the melting point or even for moderate periods of time to anywhere near the melting point of the minerals included in them, for the chondrules would have become indistinguishable from the matrix. Any adequate theory of the origin of the meteorites must account for the achondrites and the irons as well.

During the past century many scientists have assumed on more or less general grounds that the meteorites represent fragments derived from a large planet. Brown and Patterson [3] again proposed this idea, basing their conclusion on certain thermodynamic computations which they interpretated as showing that chemical equilibrium was established in meteorites under such conditions that increasing concentrations of metal phase were correlated with increasing temperatures and pressures, i.e. increasing depth in the planet. Their arguments consist of two main points. In the first case they compared the measured equilibrium constant for the reaction

$$Ni + FeSiO_3 = Fe + NiSiO_3$$

with the observed values of NiO in the silicate phase of the meteorites listed in their compilation. The observed average equilibrium constant was some 40 times

greater than the value measured by ZUR STRASSEN at about 2000°K, and thus a pressure of 3×10^5 atm is required to establish the observed concentrations at the assumed temperature of 2000°K. (Their calculation is in error by a factor of R.) They further plotted averages of groups of observed "equilibrium constants" for the above reaction against the weight percent of metal phase and found that the averages increased with increasing metal phase; thus they concluded that the higher metal phase contents represented higher temperatures or pressures or both.

These calculations assumed that the iron and nickel concentrations in the two phases represent equilibrium conditions. However, as discussed earlier in this paper, it seems certain that at least an important part of the NiO present in the oxidized part of chondrites is due to weathering and errors in analysis and in fact it was pointed out that the frequency distribution curve for NiO as given by BROWN and PATTERSON shows a maximum at 0%; thus it appears that the high value of the observed "equilibrium constant" with respect to that measured by ZUR STRASSEN has no relation to equilibrium conditions at all.

The function they have plotted against percent of metal phase is

$$C = \frac{\text{(Fe)m (Ni)sil}}{\text{(Fe)sil (Ni)m}}$$

and between points representing the average metal phase content of our low and high groups this function increases by a factor of about 2 (both with their data and our own). However, if one assumes that the NiO percentage remains constant (i.e. is due mainly to random errors) and evaluates the function one sees that it nevertheless increases between these points by a factor of 2·58, and must increase because of the greatly increased concentration of metallic iron as the metal phase increases. From Table 3 one sees that the average NiO content of the analyses listed therein which fall in our low group is the same as the average of the high group, namely 0·11%. In Table 5, analyses discarded only for high NiO, analyses which if used would fall in our low group average 0·77, and those in the high group average 0·75% NiO. There is thus no evidence for any increase of NiO in going from our low to high group. However it has been shown that the total iron and nickel content increases, and lacking dependable values for the NiO concentrations, we conclude that no information concerning equilibrium conditions can be obtained from the use of this function.

The second argument used by BROWN and PATTERSON concerns the distribution of a series of metals between the silicate and metal phases. They plotted observed "equilibrium constants" as a function of heats of formation of the oxides and obtained an average equilibration temperature of about 3000°C. The details of this procedure have been critically discussed by KLOTZ [22], who showed that even if one assumes the validity of the necessary extrapolations of great magnitude, the data actually indicate far higher temperatures and much lower pressures than obtained by BROWN and PATTERSON. The discussion by KLOTZ is quite straightforward and we shall not repeat it here.

It seems most improbable to us that the most numerous group of meteorites, namely the chondrites, could have ever been formed in a large planet because of their very intricate structure. Moreover, a large planet cannot be disrupted into

small objects except by collision with another large planet. We will neglect the possibility of an explosion of some undefined kind due to unknown explosive materials, and *ad hoc* hypotheses such as a most improbably close approach of a planet to Jupiter. But two large planets colliding with each other would have a very large kinetic energy at collision, which would be dissipated as heat. Two objects the size of the earth colliding would have to dissipate sufficient energy to raise the temperature of the whole mass to about 20,000 or 30,000°C, and thus only melted or vaporized material would be expected from such a collision. Most of this would not escape after the collision because of the high gravitational field exerted by the large amount of mass, but that which did could hardly be expected to have the complex structure of the chondrites, and since the chondrites make up more than 90% of the stone meteorites and a very substantial fraction of all observed falls, we believe this origin for the meteorites to be impossible.

In order to account for the structures of chondrites it is necessary to account for the nearly pure minerals of the chondrules and their spherical or near spherical shape. The separation of pure minerals of this kind occurs from silicate melts, and this appears to be the most probable means by which the basaltic achondrites and the minerals of the chondrules were produced. It is an old suggestion that the chondrules solidified as drops, perhaps in some cases to glasses which subsequently crystallized during longer periods of time. The growth of pyroxene minerals from one side of certain chondrules, often with glass between the crystals, is perhaps suggestive of this kind of formation*. After the chondrules are formed a method of bringing them together with mixtures of other materials, including the types of materials observed by Wahl in polymict meteorites, is necessary, and finally the materials of the chondrites must be compacted in some way into more or less solid substantial objects as they are observed, sufficiently strong to withstand passage through the atmosphere of the earth.

Kuiper [23] has pointed out that the asteroids should collide with each other with a considerable probability, about one half a collision in 3×10^9 years among 10 asteroids of larger size. Of course the number of collisions with small asteroids should be much greater. Since we know of approximately 1500 of these asteroids at the present time, some of which may have been produced from a collision of larger ones, we can expect that a very considerable number of collisions are now taking place. It also seems possible and perhaps probable that similar objects existed in the asteroidal belt in considerable numbers at the terminal stage of the formation of the earth, and in fact that the terminal stage of the formation of the asteroids themselves involved collisions of this kind.

The collision of a small asteroid with a larger one might be thought to resemble a collision of an object with the surface of the moon such as those that produced the craters on the moon, a great splash of materials producing a circular wall about the point of collision. However, there would be two important differences. First, no object can hit the moon with a velocity lower than about 2·3 km/sec., that is, the escape velocity of the moon, if it falls freely from a great distance, while the escape velocity of an asteroid of 100 km radius would be of the order of

* In some cases the crystalline fibres appear to radiate from a point outside of the chondrule, a fact which is difficult to explain by any petrological hypothesis.

140 metres/sec. (Lunar collisions of lower velocity are possible but the absolute minimum is the circumsurface velocity of 1·7 km/sec.) Hence collisions of smaller asteroids with the surface of a larger asteroid can take place with a relatively low collision velocity. The velocity of an object moving in a circular orbit at 2·3 astronomical units from the sun would be 19 km/sec., and it could be expected that some reasonable fraction of this velocity, say perhaps 10%, might be the relative velocity of approach of two asteroids in a collision because of inclination of orbits and different eccentricities of orbits. In the second place, due to the small gravitational energy of the asteroidal body, a collision of a rather small asteroid with a larger asteroid might break up the larger one to a very substantial degree. Thus a 10 km radius asteroid of density 3·5, moving at 3·7 km/sec. relative to an asteroid of 100 km radius and the same density, would possess sufficient energy to completely scatter the larger asteroid to an infinite distance if none of the energy were converted into heat. Of course a substantial fraction of the energy would always be converted into heat, but one sees that there exists the possibility of the asteroid being broken into large pieces of rubble even if the pieces are not scattered to great distance.

Nininger has found iron-nickel spherical objects in the neighbourhood of the Arizona meteor crater*. These evidently fell as a molten iron rain during that collision. It may be that silicate droplets were also formed. Perhaps it is reasonable to assume that chondrules originated from materials melted in collisions of this kind. If so, the moon must have both iron and stone chondrules distributed on its surface, and it seems probable that collisions between asteroids would produce some degree of melting of the same kind, thus producing chondrules in these collisions.

Collisional processes of the kind described should produce a rubble-like structure on the surface of the asteroids. Great splashes of material would occur which because of the low gravitational field would be spread over the whole surface of the asteroid, and probably to some extent, escape from the asteroid as well. In the neighbourhood of the collision large drifts of rubble containing chondrules should be produced out of the surface materials of the asteroid and from the materials of the colliding bodies. Great masses of finely broken up silicates and bits of iron should occur. Drifts of black material might become mingled with grey material. The polymict character of the meteorites might well originate in these banks of rubble on the surface of asteroids. It seems to us that the mixing of different types of chondritic and achondritic material must have occurred before the compression into these dense compact objects occurred.

We will make the following postulate of the course of events: As proposed by Urey [24], we assume that the accumulation of the great body of the asteroids took place at relatively low temperatures, thus preserving the more volatile constituents from evaporation. Many elements would have been lost very completely had such an accumulation process taken place at high temperatures, and

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* *Personal communication.* He also states that he has found a few spheroids which appear to be composed of metal, but turn white and become slightly porous when boiled in nitric acid. The solution gives a strong positive test for nickel; thus he assumes that small particles of metal were present in the silicate spheroids. These facts are suggestive of silicate chondrules covered with metal.

the distribution of the elements in the upper part of the periodic table does not seem to justify such a large scale fractionation as might be expected at such temperatures. On the other hand, in order to account for the substantial bodies of iron in meteorites, and for the iron objects which ploughed out the grooves on the moon, it is necessary to assume some process by which such masses of iron could accumulate. A high temperature process produced by the adiabatic compression of the gases of the proto-planets from which the asteroids were formed would now heat the surface of the objects, reduce iron in the surface, and evaporate silicates from the surface by processes which have previously been discussed [21]. During this stage it can hardly be expected that the chemical processes taking place all over the surface of the asteroid would be uniform, for the object may well have been not completely spherical since its gravitational field was low, and in the melting process silicates would flow from the higher regions to the lower thus producing quite different chemical conditions at different points. Probably considerable evaporation of the silicates occurred from the surface, but toward the end of the process one could expect a rather thin layer of silicate beneath which may have been a rather ill-defined and poorly separated layer of iron sulphide, and below this a layer of metallic iron-nickel alloy, and finally in the interior of the asteroid relatively unchanged non-volatile cosmic material, perhaps with water and other volatiles imbedded in it to some degree. As the heating process terminated by the dissipation of the gases of the proto-planet, perhaps by light pressure from the sun, a layer of molten silicates would be left on the surface to cool slowly and crystallize. This layer can be postulated to be the origin of the achondrites and the origin of the pure minerals in the monomineralic chondrules of the chondrites. The layer of iron can be postulated to be the origin of the iron meteorites, and the stony irons could be derived from an incompletely separated mixture of iron and silicates.

The data presented in this paper indicate that there are two distinct types of chondrites which differ mainly in their nickel-iron content and the oxidation state of the iron. We have been unable to conceive of an arrangement in a single large planet which could furnish these two groups and the iron meteorites upon breaking up and which could have resulted from processes that have a reasonable probability of occurring. Vogel and Heumann [32] have recently studied the dependence of the formation of the Widmanstätten structure in iron upon pressure and concluded that the iron meteorites must represent fragments of a small object whose internal pressure was not greater than 50,000 atmospheres. Such an object composed of chondritic type material would have a diameter of the order of 1700 kilometres, namely about the same as the moon. The object could of course have been larger if the iron meteorites were derived from a layer near the surface, as we believe, rather than from the core. Since the two types of chondrites can not be related to each other either by a mixing process or an oxidation-reduction process, but require both, it is our belief that they must have been derived from two different asteroids. On one of these iron was concentrated relative to silicates, and also more reduction (or less oxidation) of the iron took place.

Urey [24], [25], discussed the different proportions of iron to silicate in the

terrestrial planets and attributed these to the effects of evaporation of the silicates during a high temperature stage in their formation. Though this is not the only process that can be imagined in order to account for the different amounts of iron-nickel in the two groups of chondrites, nevertheless it appears to us to be a reasonable postulate. It presents a method by which the silicates are preferentially removed, and in this case it would appear that the process has taken place to a larger degree in the case of the high iron group asteroid. We shall not attempt to give a detailed picture of the evolution of all the various types of meteorites here; we wish only to outline the general indications we have obtained from the data.

Table 12 gives the average normative composition in weight percent of the chondrites in our low group, calculated according to the procedure suggested by WAHL [16]*. The table also shows the normative composition of the average of 12 superior analyses of white chondrites, calculated by WAHL [16]. The agreement of the norms is quite close and emphasizes again the similarity of the white chondrites as a group to the average low group chondrite.

Using the best available values for mineral densities†, the density of the low iron group of chondrites calculated from the normative composition is 3·52, in very good agreement with the observed mean density of 3·51. UREY [23] has estimated the density of the moon at ordinary temperatures as 3·47, thus in rather close agreement with this low iron group in density. It would appear that the same sort of fractionation of the elements has occurred between the two asteroids that produced the chondritic meteorites as has occurred in the formation of the terrestrial planets, where the moon is the object of lowest density. Thus the original postulates made by UREY appear to be justified in this way.

During the evaporation process there must have been a layer of generally basaltic composition on the surface derived from the melting of the ultrabasic primordial cosmic material. Iron would also enter the evaporating layer since it is a constituent of the silicate phase; thus some iron would be evaporated and some would be reduced and sink to form a layer of molten nickel-iron. Iron sulphide tended to accumulate above the iron and below the silicate, but most of it was reduced. In the end stage there were various types of layers of different material; the metallic iron must have been present as a definite layer or as fairly large irregular local accumulations.

Following this stage came the stage of collisions between a large asteroid and smaller ones in which the surface was broken up, chondrules were produced from the minerals of the basaltic layer, and the whole surface of the asteroid was converted to a rubble, partly composed of the minerals of the asteroids and partly of those of the colliding objects which are very difficult to define. For reasons following from the elementary abundances of the elements to be discussed below, it appears that the differentiated layers of basaltic material and metallic nickel-iron were relatively thin and that most of the materials of the chondrites came from a more extensive layer.

* Here however we have averaged phosphorus tabulated as P into P_2O_5 (except when both P and P_2O_5 are given) as mentioned in the footnote to Table 2.

† Densities for the pure iron and magnesium meta-silicates were taken from the *International Critical Tables*; for the pure ortho-silicates from DANA'S *Textbook of Mineralogy* (John Wiley and Sons, 1932).

Table 12. *Average normative composition in weight percent of Low Group chondrites*

Minerals	*Low Group Chondrites*	*Average of 12 White Chondrites* (Wahl)
$K_2O.Al_2O_3.6SiO_2$	1·06	1·16
$Na_2O.Al_2O_3.6SiO_2$	7·96	8·38
$CaO.Al_2O_3.2SiO_2$	2·36	2·20
$FeO.SiO_2$	7·02	7·36
$FeO.TiO_2$	0·21	0·24
$MnO.SiO_2$	0·49	0·51
$CaO.SiO_2$	2·53	2·26
$MgO.SiO_2$	15·92	16·50
$2FeO.SiO_2$	15·39	13·85
$2MgO.SiO_2$	31·67	30·67
$FeO.Cr_2O_3$	0·64	0·71
$3CaO.Na_2O.P_2O_5$	0·58	0·63
Fe	7·04	7·76
Ni	1·06	1·25
Co	0·07	0·07
FeS	5·77	6·97
	99·77	100·52

Finally, perhaps 10^9 or more years later, a collision between two of the larger asteroids occurred. A head-on collision between two large asteroids of this kind is difficult to describe without experience in regard to much larger collisions than those we have seen on the earth. The usual formula for the pressure generated when two objects of this kind collide is

$$P \cong \rho v^2$$

and with ρ and v equal to 3·5 gcm^{-3} and 2×10^5 cm sec^{-1} the pressure would be of the order of 10^5 atmospheres. Thus in the region of contact we could expect sufficient pressures to compact the rubble-like material into solid objects, and these objects would have a structure, it seems, similar to those of chondrites. Larger objects of the original basaltic material which solidified on the asteroid would appear as achondrites. Iron objects would be likely to be scattered relatively free of silicate materials because of the marked difference in density of the metal and silicate phases which would develop strong forces between these two types of materials in any collision between objects containing both these materials. Of course, a large fraction of the asteroids would probably be dissipated as very friable material, so that the surface materials at the back sides of the collisions and at the edges would probably not be subjected to sufficient pressures to compact them into solid objects at all. It would seem likely that the materials of the two asteroids at the point of contact would remain relatively unmixed, and thus any difference in chemical composition of the two asteroids would appear in the chondrites produced. The data on the relations of the polymict brecciated meteorites to our two groups indicate that the polymict characteristics antedate the

collision of the two larger asteroids. Thus it would seem reasonable that the two types of chondrites which are discussed in this paper and shown in Fig. 1 may owe their origin to a difference in composition of the two asteroids, and this difference in composition in turn arose from the different chemical processes to which they were subjected due to differences in size, temperatures, pressures, time of heating, etc.

The postulated course of events outlined above would seem to be able to account for all the various characteristics that we observe in meteorites. At the same time it could not be maintained that the process is necessarily a unique one, and undoubtedly, the true process was even more involved for we can only outline roughly the actual events. We shall use this postulate as a working one for further discussion.

9. Abundances of the Elements

In this paper we are assuming that the chondrites represent a fairly good average of the non-volatile fraction of the elements which produced the asteroids. We base this upon our discussion of the possible origin of these objects. This possible origin, however, emphasizes that both groups of chondrites cannot be expected to represent this average sample, since they are quite different with respect to the siderophile elements.

In Table 13 we give the atomic abundances of the elements in the low and high iron groups of chondrites and the average abundances in all analyses in Table 2. For the purpose of this table the averages given in Table 2 have been corrected as follows: calcium from CaS, chromium from Cr_2S_3, and sulphur from both of these compounds have been averaged into the tabulations, and phosphorus tabulated as P has been averaged in as previously described. Silicon has been normalized to 10.000 in each group of abundances. The table also shows the enrichment between the high and low group abundances, taken as positive if the element is concentrated in the high group with respect to the low group.

These enrichment factors show first of all that the siderophile elements are strongly concentrated in the high iron group, nickel and cobalt being even more concentrated than iron. This higher enrichment factor for nickel expresses the fact that the differential material between the low and high groups is enriched in nickel with respect to the bulk composition of the low iron group. Cobalt shows an enrichment factor similar to that of nickel but the precision of cobalt determinations may not be good enough to justify any certain conclusion.

If it is indeed true that the chemical evaporation process has operated more effectively in the case of the high group chondrites, then the low group is the better cosmic sample of the two, but this argument also leads to the conclusion that the amount of the siderophile elements in this low iron group is larger than it should be. We can therefore take the abundances of the elements in the low iron group of chondrites as the best we have available, but with the probability that the siderophile elements are still somewhat too abundant. Moreover, since some iron can be lost by evaporation from the silicate phase while the more noble metals remain in the molten iron layer, we can expect that the abundances of the metals more noble than iron are too high by a larger factor than in the case of iron.

Fig. 6 shows the frequency distribution of Cr_2O_3 in the low and high groups. The figure indicates that the data with respect to this oxide are of such poor precision that we should attach no significance to the high fractionation given in the table of abundances.

Sulphur is slightly more abundant in the high iron group relative to silicon: the enrichment is just on the border of the order of magnitude that we would consider significant. If the enrichment is real it may reflect the protective effect of the higher density of ferrous sulphide, which would allow it to sink below the evaporating surface.

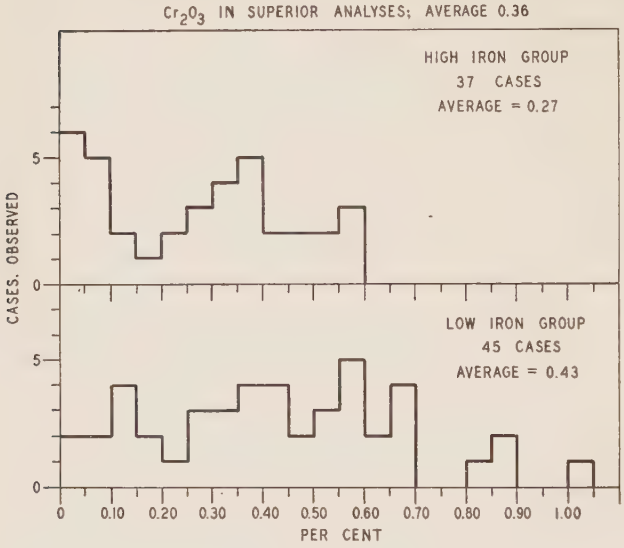

Fig. 6. Frequency distribution of Cr_2O_3 in low and high iron groups of chondrites.

The lithophile elements show no significant effects of fractionation with respect to the two groups except perhaps in the case of calcium. If all constituents of the silicate layer were evaporated no fractionation between the lithophile elements would occur, since the silicates of the chondrites would be derived only from the relatively undifferentiated materials below the iron layer. Since the basaltic achondrites appear to represent material of the type we believe would have existed in the surface layer of an asteroid, it seems probable that some residue was left over from the evaporation process. Urey has discussed elsewhere the relative volatility of the elements in the present of cosmic proportions of gases [21], [24], [25] and we shall not repeat the discussion here. The thermodynamic data indicate that calcium is the least volatile of the lithophile group in the presence of hydrogen and should be enriched in the residue; thus the enrichment of 12% shown in Table 13 may be significant. It is interesting to note that two achondrites, Angra dos Reis and Nakhla, show extreme amounts of calcium oxide. It is difficult to account for such a high abundance of calcium relative to magnesium and aluminum by any melting processes, and hence these may represent chance survivors from a small patch of evaporation residue rich in calcium oxide.

We wish to emphasize that we regard the lines of evidence discussed in this section as suggestive but far from conclusive relative to the details of the postulated chemical fractionation process. In fact we believe it probable that some meteorites do not belong to our proposed process at all, since many collisions between smaller bodies should be occurring and thus quite specialized objects should be produced. The carbonaceous chondrites are difficult to account for by our process. Cold Bokkeveld contains relatively volatile carbon compounds and water*,

* G. Mueller, personal communication.

and at the same time contains 23·26% of oxidized iron and only 2·50% of metallic iron. Our theory requires that this increased total iron content was produced by the high temperature evaporation process which produced metallic iron. Following this water must have been introduced which oxidized the metallic iron almost completely and in this stage both the water and carbon compounds were introduced. Or, is Cold Bokkeveld the original cosmic material and are our groups composed of objects produced from such material by some other chemical fractionation process?

Table 13. *Atomic abundances of the elements in chondrites*
Silicon = 10,000

	Low Group	*High Group*	Δ %	*Total Average*
Oxygen	34,760	33,882	− 2·6	34,386
Sodium	509	490	− 3·8	500
Magnesium	9,261	9,444	+ 2·0	9,335
Aluminum	778	769	− 1·2	774
Silicon	10,000	10,000	—	10,000
Phosphorus	47	42	−12·6	45
Sulphur	1,000	1,100	+10·0	1,041
Potassium	58	59	+ 1·1	58
Calcium	532	595	+12·0	558
Titanium	21	23	+ 8·8	22
Chromium	87	63	−37·9	76
Manganese	57	54	− 6·0	56
Iron	6,084	8,498	+39·7	7,091
Cobalt	17	29	+68·6	23
Nickel	274	476	+73·3	360
Fe/Ni	22·17	17·87	24·1	19·72
Fe/Ni (weight %)	22·07	17·01	−23·9	18·71

10. Summary and Conclusions

In this discussion of the origin of meteorites we have not attempted to give a detailed picture of the various mechanisms that have operated in the processes we have postulated. Rather, we have tried to present a general outline on the basis of the most plausible construction we can correlate with our observations, and we list herewith those observations and implications which we feel are most germane to the problem at hand.

1. Analyses of chondrites selected on the basis of maximum reliability show that two groups of chondrites exist which differ in their percent of total iron and in the proportion of oxidized to reduced iron. Some elements show different relative abundances in these two groups.

2. The structure of the chondrites indicates that they are agglomerates of silicate fragments, chondrules, and metallic nickel-iron. Moreover, there are indications that the brecciation and mixing processes which formed these objects operated within and not between the two observed groups of chondrites.

3. On the other hand, the achondrites generally possess structures more characteristic of terrestrial rocks in which melting processes have been dominant.

4. There exists to our knowledge no real evidence to indicate that all meteorites are derived from a single large parent planet, and in fact astronomical and physical considerations strongly imply that such was not the case.

5. The existence of iron meteorites necessitates the postulate that, whatever the structure of the parent object or objects, a segregation and coalescence of iron-nickel occurred which was maintained until the meteorites were produced. The small size of the irons and the inclusion of iron sulphide nodules indicate that they were derived from a layer not over a few metres in thickness or localized aggregates of such size rather than from a completely segregated core. The presence of metallic iron in the achondritic stone meteorites also indicates that complete segregation did not occur.

The picture we have presented of the separate development of two asteroids with different chemical compositions and their subsequent genesis of meteorites by a disruptive collision is the only concept we have been able to fit to the pattern of observations we have to work with. This picture is by no means complete, nor do we wish to maintain that it is correct in every detail. It is of course much easier to devise processes to produce desired effects than to predict to what degree the various processes will operate. Nevertheless we feel that the general postulates made in this paper are as consistent as we can expect with the present meteoritic data.

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Sur la meteorite de Guidder

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ABSTRACT

On the evening of January 7th, 1949, a meteorite shower was observed near Guidder in the Cameroons. Two stones were recovered and presented to the Natural History Museum at Paris. In this paper a general description of the stones, the results of microscopic examinations of thin sections, and chemical analyses of the silicous and metallic phases are given.

En 1951, Ed. Roch, chef des travaux pratiques de géologie à la Sorbonne, de retour d'une mission au Cameroun, faisait don au Muséum National d'Histoire Naturelle de Paris, d'une météorite pierreuse tombée en Janvier 1949 à Guidder (Cameroun).

Peu de temps après, l'enquête faite par M. F. Callot, chef du Service des Mines du Cameroun, lui a permis d'envoyer au Muséum une seconde pierre provenant de la même chute. Le chef de la subdivision où le phénomène a eu lieu, a communiqué ses observations que nous reproduisons en entier:

> "Ce météore est tombé le 7 janvier 1949 vers 18 h. 45. Avant sa chute, sa projection était orientée NNW-SSE. Je l'ai personnellement aperçu à ce moment de Masabay, village situé à 35 k. environ au NW de Guidder. Son point de chute se situe environ à 6 ou 8 km au SE de cette localité.
>
> "Ce phénomène semble avoir fait explosion en l'air; en effet il apparut d'abord comme un globe incandescent suivi d'une trainée d'étincelles, puis il éclata en nombreux fragments également incandescents. Quelques secondes après, le bruit de cette explosion parvint très assourdi. Aucun fragment trouvé au sol ne dépassait un volume d'un décimètre cube."

Nous exprimons ici notre gratitude à M. Ed. Roch et à M. F. Callot.

Caracteres Exterieurs

Il ne s'agit pas d'un spécimen ou de plusieurs fragments d'un spécimen, mais d'un essaim de pierres dont deux seulement ont été remises au Muséum, pesant respectivement 476 gr (poids initial, le poids actuel étant ramené à 376 gr) et 492 gr.

La première (Fig. 1) est grossièrement conique, comporte 5 faces, la seconde (Fig. 2) a 5 faces également convergentes vers un sommet tronqué (Fig. 1 and 2) Elles sont reconvertes presque complètement d'une croûte noire (Fig. 3), très fine, laissant apparaitre dans quelques cassures affectant les arêtes ou les angles, la couleur gris-clair de la météorite. La croûte noire brunâtre à l'éclat gras est creusée de place en place par des piézoglyptes (Fig. 1 et 2) peu profonds, aux contours sphériques ou légèrement ovoïdes. Au fond de certains piézoglyptes on aperçoit un large grain métallique. Mais le métal apparait aussi, bien que rarement, en saillie. La densité est de 3,92.

La surface polie permet de voir la teinte gris-clair de la météorite et les nombreux chondres de dimensions variées atteignant parfois plusieurs mm. Les

grains métalliques de toutes tailles sont distribués inégalement, réunis par places en grosses taches où l'on distingue facilement le fer nickelé presque blanc, très brillant, occupant la partie centrale et la troilite lui faisant bordure, un peu rugueuse et jaune. Localement on aperçoit des traces de rouille autour des éléments métalliques ou au milieu de la partie silicatée.

La structure n'est pas bréchiforme mais la richesse en chondres, faiblement réunis par un ciment à grain fin, résultant de l'écrasement, rend la météorite peu cohérente et susceptible de s'effriter sous une pression un peu forte.

Etude Microscopique

L'étude au microscope met en évidence une richesse exceptionnelle en chondres: entiers ou fragmentaires, gros ou petits, parfois agglomérés par deux (Fig. 5) ou par trois; ils sont séparés par un amas de grains et de cristaux très petits. La comparaison avec d'autres chondrites rapproche ce type des chondrites dites "globulaires" ("kristalline Kügelchenchondrite" de Brezina).

La composition minéralogique est simple: péridot prédominant ortho-et clino-pyroxènes ferro-magnésiens, très peu de diopside et de feldspath, de rares agrégats de merrillite, ainsi que de petites inclusions de *chromite* dans les feldpaths (Fig. 7) et dans les péridots.

Enfin le ferro-nickel et la troilite représentent la partie métallique.

A. Minéraux non métalliques

Le *péridot* constitue rarement des cristaux isolés ayant leurs formes propres; inclus dans l'hypersthène, ils sont arrondis. Le plus souvent ils entrent dans la composition des chondres. Extrêmement fissuré, riche en inclusions, ils sont en général légèrement colorés en brun. De nombreuses mesures (platine de Fedoroff, lumière monochromatique Na) ont permis de préciser qu'il s'agit d'une variété à signe potique négatif, l'angle 2V ne dépassant pas 82°.

L'hypersthène, second minéral par ordre d'abondance constitue des baguettes courtes ou allongées suivant l'axe vertical, ou des grains, mais le plus souvent il forme des chondres radiés excentrés. On le voit aussi associé à axes parallèles à l'olivine. La biréfringence est faible, l'angle 2V (p. de. F) atteint 68°.

Très rarement on rencontre le clinohypersthène, qui possède une biréfringence plus faible que celle de l'hypersthène, de fines bandes de macles polysynthétiques à exctinction oblique et le plan des axes disposé transversalement.

Nous n'avons pas trouvé de *diposide* en cristaux isolés, mais seulement en baguettes bordant l'hypersthène, ou associé à l'olivine dans les chondres.

Il y a peu de *feldspath* dispersé comme élément interstitiel dans les chondres ou entre les minéraux, souvent en amas de petits grains, sans macles visibles, ou aux macles fines et ternes. L'étude à l'aide de la platine universelle s'avère impossible. Nous avons pu constater sur une section perpendiculaire à la bissectrice *ng* que *np* est nettement plus bas que l'indice du baume du Canada, *nm* l'est moins distinctement. On verra que l'analyse chimique met en évidence un feldspath presque alcalin, très peu calcique. Les macles presque toujours existantes, comme on peut s'en rendre compte à la pl. de Fed. sont difficiles à utiliser à cause de l'angle d'extinction très petit, de la biréfringence extrêmement faible, de l'absence de

Fig. 1

Figs. 1, 2. Aspect extérieur des deux pierres de Guidder. On voit nettement les piezoglyptes

Fig. 3. Croûte en lumière naturelle. Gross. 60

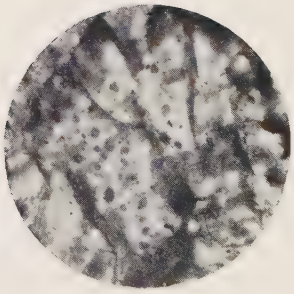

Fig. 7. Petits cristaux de chromite inclus dans le feldspath. L.N. Gross. 520

clivages et de la taille minuscule des grains. Nous ne pouvons pas dans ces conditions tirer partie des courbes données par E. Preuss (1951) pour les feldspaths formés à haute température. A en juger d'après l'analyse chimique, c'est une albite potassique, si toutefois la soude ne se trouve dans un autre silicate. Rappelons pourtant que W. Wahl (1950) admet que les alcalis des météorites se trouvent principalement dans les feldspaths.

Rarement le feldspath se présente en amas de grains de dimensions plus considérables (1 mm) dont l'orientation optique est très variable; ils sont remplis d'inclusions de minéraux transparents ou opaques.

Le feldspath de la chondrite de Guidder passe parfois à la *maskelynite* qui se rencontre aussi isolément.

Chondres

La meilleure façon de se rendre compte du grand nombre de chondres ainsi que de la variété de leur structure, est de regarder la plaque mince par transparence à la loupe. En effet, les chondres sont parfois tellement volumineux qu'ils occupent tout le champ du microscope.

C'est particulièrement le cas des chondres polysomatiques composés d'olivine seule (appelés improprement "porphyriques") dans lesquels les grains et les cristaux sont entourés d'un amas de petits grains appartenant à la même espèce, et résultant d'un écrasement de l'ensemble (Fig. 4).

La chondrite de Guidder est remarquable par la fréquence des chondres agglomérés. La Fig. 5 montre deux chondres jumeaux, de dimensions différentes, et d'une composition identique. Deux anneaux externes d'olivine, perpendiculaires à la bissectrice *ng*, dont le contour dessine le chiffre 8, entourent les deux individus. Ils s' éteignent simultanément sur la quasi totalité de leur étendue mais changent d'orientation à l'une des extrémités du grand chondre où le minéral est perpendiculaire à l'axe. Une mince bordure de poussière métallique souligne la couronne interne des anneaux. Le plus petit des deux chondres est formé par des grilles d'olivine de la même biréfringence que l'anneau. Un seul cristal d'olivine se trouve à l'intérieur du grand; de place en place des grains de feldspath sont coincés dans les intervalles. Les deux anneaux sont bordés à l'extérieur par une zone presque continue de cristaux allongés d'hypersthène qui s'adaptent exactement aux contours des couronnes soit en se tordant soit en formant des gradins concentriques. Un chondre identique par la forme est figuré dans Tschermack (1885) Pl. XIX, Fig. 4. L'olivine des anneaux est remarquable par sa limpidité tandis que les grilles et les grains internes sont troubles et bruâtres à cause d'une grande quantité d'inclusions. On pourrait en conclure à l'antériorité de cristallisation des anneaux par rapport à ce qu'ils renferment.

Les chondres péridotiques en grilles continues ou annelées sont très fréquents. Leurs baguettes sont séparées entre elles par de petits lits de matière vitreuse riche en poussière métallique, cédant parfois la place au feldspath. Quant les baguettes sont très fines, elles manifestent une tendance à s'orienter en éventail de très faible ouverture. Dans un grand chondre d'olivine, les baguettes annelées suivent une circonférence en zones concentriques disposées en gradins.

Il n'est pas possible de décrire toutes les variétés de chondres de cette météorite.

Il parait néanmoins intéressant d'attirer l'attention sur le cas des chondres pyroxéniques excentrés en éventail.

Les chondres de pyroxène orthorhombique sont le plus souvent bacillaires et excentrés. Il arrive qu'ils se terminent par un cristal unique du même minéral. Fréquemment ils sont comme soulignés par un pointillé de grains arrondis ou allongés d'olivine. Les fibres d'hypersthène sont quelquefois associées à des baguettes d'olivine à axes parallèles ou transverses.

Tenant compte de la structure fibreuse des pyroxènes, on peut émettre l'hypothèse d'une cristallisation radiée divergente, ayant rempli des nucléoles à partir d'un germe fixe au bord de celles-ci.

B. Analyse chimique de la chondrite de Guidder (*La partie silicatée par Jakob de Zürich et la partie métallique par* H.B. Wiik *de* Helsinki)

SiO^2	41,73	Or	1,11		
Al^2O^3	1,94	Ab	8,38	Feldspaths	9,77
Cr^2O^3	0,15	An	0,28		
FeO	15,96	$CaSiO^3$	3,94		
MnO	0,44	$MgSiO^3$	2,60		
MgO	26,43	$FeSiO^3$	1,06	Pyroxène monoclinique	8,76
CaO	2,14	$FeTiO^3$	0,38		
Na^2O	1,05	$MnSiO^3$	0,78		
K^2O	0,21	$FeSiO^3$	5,81	Pyroxène	19,21
TiO^2	0,14	$MgSiO^3$	13,40	orthorhombique	
P^2O^5	0,23	Mg^2SiO^4	35,07	Olivine	52,10
H^2O+	0,57	Fe^2SiO^4	17,03		
H^2O-	0,09	Chromite	0,22	Chromite	0,22
		Merrillite	0,60	Merrillite	0,60
	91,08				
Fe	4,37	Fe	4,37	NiFe	5,30
Ni	0,93	Ni	0,93		
Fe	2,21	FeS	3,48	Troilite	3,48
S	1,27				
Total	99,86				

L'analyse chimique de la chondrite de Guidder est caractéristique de la majorité des chondrites: richesse en MgO et FeO, pauvreté en alumine. Etant donné la faible teneur en silice pour ce type pyroxéno-péridotique, l'olivine prédomine sur le pyroxène. D'après la classification de A. Lacroix (1906) ce serait une chondrite pyroxéno-péridotique oligo-sidérifère.

C. Partie métallique

L'étude microscopique en sections polies a montré la présence de deux minéraux. L'un d'eux forme généralement de larges plages tabulaires aux contours souvent irréguliers, la couleur est jaune crème très pâle tirant sur le blanc; les grains sont soit indépendants (20 à 60 μ) soit en agrégats de granules allotriomorphes, le pouvoir réflecteur est de 40% environ. En lumière polarisée on observe une nette biréflectence accusant des macles d'allure polysynthétique (Fig. 8), les individus étant disposés tête bêche et aux axes alignés à 15° près.

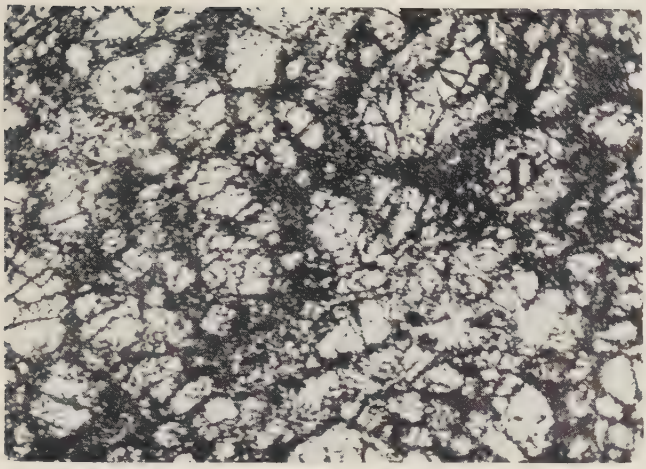

Fig. 4. Partie d'un chondre péridotique: grains fissurés d'olivine, entourés par des petits grains de trituration du même minéral. L.N. Gross. 90

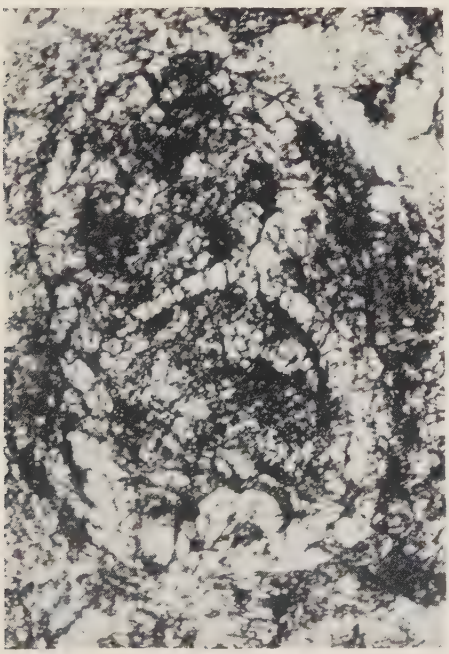

Fig. 5. Chondre double péridotique. N^+. Gross. 60

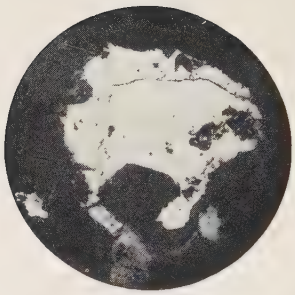

Fig. 6. FeNi bordé de troilite.
Lum. réfl. Gross. 75

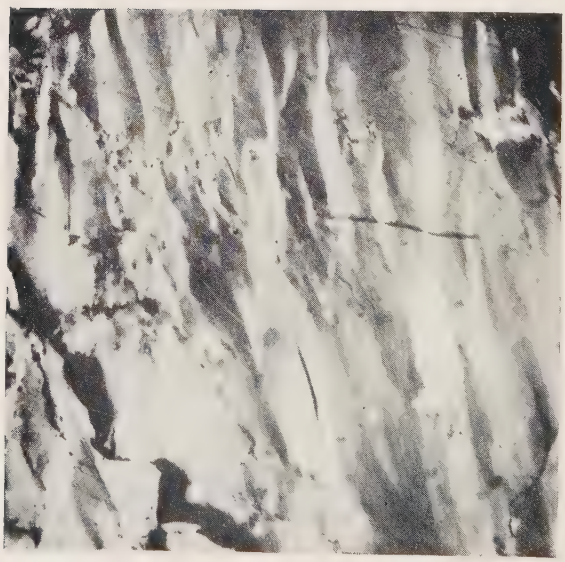

Fig. 8. Macles polysythétiques dans la troilite.
Lum. réfl. N⊦. Gross. 100

Ces caractères correspondent á ceux de la *troilite*.

Le second minéral métallique est en grains minuscules, allant rarement jusqu'à 100 μ, le plus souvent isolés. Fortement réfléchissant, il a un éclat blanc d'argent. En lumière polarisée, on voit qu'il est isotrope; il semble donc appartenir au groupe des ferro-nickels, métaux normaux dans une chondrite.

Au fort grossissement, on remarque que ce ferro-nickel représente une association de deux minéraux, l'un bordant l'autre ne se distinguant que par une légère différence d'intensité de leur éclat brillant blanc. Souvent la troilite est associée au ferro-nickel et l'entoure (Fig. 6)—confirmation de l'ordre normal de cristallisation: 1) métaux natifs, 2) sulfures.

Etude chimique

Des grains de ces deux minéraux, isolés sous le microscope, ont été soumis à l'analyse spectrale: 15 mg, Arc 110 V, 2–15 Amp 30 sec.

$$\left.\begin{array}{ll} \text{Troilite:} & \text{Fe Ni}^{+++}\ \text{Cu}^{+++}\ \text{Ag}^{+} \\ \text{Ferro nickel:} & \text{Fe Ni CO}^{+++}\ \text{Cr}^{+++}\ \text{Cu}^{++} \end{array}\right\}\ \text{Ga}^{+}$$

La troilite a pu être isolée en assez grande quantité pour une analyse rudimentaire, dont le résultat: Fe 66% $\pm$ 0,50; S34% $\pm$ 0,20 confirme la formule Fe_6S_6 admise pour ce sulfure.

Etant donné que dans la méthode adoptée par H. B. Wiik (1950) pour analyse chimique, les métaux natifs sont extraits du mélange métallique à l'aide de Cl^2Hg, il ne rentre dans la solution obtenue aucun élément sulfuré et c'est dans cette solution que le Fe et le Ni sont dosés.

Pour la météorite de Guidder nous obtenons un ferro-nickel contenant Fe 4,37% et Ni 0,93% soit un ferro nickel à 17% de Ni, alliage naturel du groupe de la taenite.

Sur une autre fraction métallique est dosé le S (le S de CaS est extrait à l'acide acetique de l'ensemble des fractions métalliques et silicatées) et recalculé en FeS à raison de Fe^6S^6—composition normale de la troilite. Pour la météorite de Guidder cela donne une teneur pondérale de 3,48% de troilite.

Il nous a semblé intéressant de calculer les proportions volumétriques relatives de ces deux minéraux.

$$\text{d.—Troilite} = 4{,}65;\ \text{d.—(Fe Ni 17\%)} = 8$$

$$\text{rapport du Vol de la troilite au Vol de Fe Ni} = \frac{0{\cdot}748}{0{\cdot}666} = 1{\cdot}12$$

Le rapport des volumes étant 1,12 nous avons essayé de rechercher une confirmation à l'aide de la platine intégratrice*.

Les mesures faites en immersion à la platine intégratrice nous donnent $\frac{\text{Vol. Tr}}{\text{Vol. FeNi}} = 1$. La différence de 12% que l'on constate entre le rapport des volumes calculés sur la base de l'analyse et le rapport des volumes mesurés

*Integrating micrometer. (Ed.)

semble satisfaisante. Elle rentre dans la limite des erreurs de mesures additionnelles. On peut donc conclure que la météorite de Guidder renferme un pourcentage gravimétrique de 5,30% de taenite à 17% de Ni et 3,48% de troilite Fe^6S^6.

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Deuterium content of natural waters and other substances

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ABSTRACT

A mass spectrometric method for the accurate determination of the hydrogen-deuterium ratio has been developed. It is possible to determine this ratio to $\pm 0{\cdot}10\%$ using material of "normal abundance", i.e., 1 part D in 6700 parts H. Samples as small as 0·1 mg H_2 (0·001 ml H_2O) can be run. Natural evaporation and condensation that have been shown to fractionate the oxygen isotopes also fractionate the hydrogen isotopes. The ratio of these two fractionations is equal to the ratio between the ratios of the vapour pressures of H_2O/HDO and of H_2O^{16}/H_2O^{18}.

Ocean waters range from 0·0153 to 0·0156 mole % deuterium, whereas fresh waters of the United States range from 0·0133 to 0·0154 mole % deuterium. A measurement of Yellowstone Park fumarole gases gives a minimum temperature of 400° for the equilibrium $H_2O + HD = HDO + H_2$ in the gases.

The stable hydrogen isotopes, protium and deuterium, are of great interest geochemically, as they are separated or fractionated by geological or cosmological processes to a larger extent than any other pair of stable isotopes. Therefore they can serve as a useful indicator to help reconstruct the conditions under which such processes have occurred. The object of this research was to develop a method for determining the H/D ratio in milligram amounts of water or in other materials containing hydrogen. The accuracy of the method was to be better than $\pm 0{\cdot}5\%$ of the ratio in water of normal deuterium abundance (1 part D in 6700 parts H); e.g., $1{\cdot}000 \pm 0{\cdot}005$ parts D in 6700 parts H.

It was decided that the only practical method of analyzing large numbers of small samples with the accuracy desired was by the use of a mass spectrometer. The first approach was the conversion of a water sample to HCl by reaction with $SiCl_4$. The HCl was then passed into a Nier-type (6-in., 60°) mass spectrometer and the ratio of the peaks at mass 38 (H^1Cl^{37}) and mass 39 (H^2Cl^{37}) was determined. Great difficulty was encountered in removing the impurities that gave a peak at mass 39—most hydrocarbons containing more than 3 carbon atoms give a large peak at mass 39 $(C_3H_3)^+$.

The next approach was the determination of the H/D ratio directly on hydrogen gas made by the reaction of a water sample with hot zinc. A new mass spectrometer tube was constructed, based on a design by Nier†, in which an additional collector tube was joined to the usual 6-in., 60° spectrometer tube in such a way that it would collect the mass 2 ion beam while the usual collector simultaneously was collecting the mass 3 ion beam.

The voltage developed by the mass-2 ion beam current flowing through a $1{\cdot}5 \times 10^{10}$-ohm resistor was used to buck out the voltage developed by the mass-3 ion beam current flowing through a $1{\cdot}5 \times 10^{11}$-ohm resistor. The difference

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† A. O. Nier, personal communication.

voltage was amplified by a vibrating reed electrometer and recorded by a Brown Electronik strip chart recorder.

In accordance with a suggestion of Mark Ingram* the defining slits in the Nier-type ion source were both enlarged from 0·010 in. and 0·020 in. to 0·040 in. to increase the ion beam intensity, and a repeller electrode was placed in the shield box parallel to the plane of the slit plates. The voltage on the repeller electrode was variable from 0 to 10 volts negative in respect to the shield. This repeller plate established an accelerating field inside the shield box, which repelled the H_2^+ ions toward the shield, thus aiding in the removal of the H_2^+ ions by passing them through the slit in the shield. It is necessary to remove the H_2^+ from the shield box as rapidly as possible to minimize the formation of the H_3^+ ion, which will be collected on the mass-3 collector together with the HD^+ ion. A discussion of the formation of the H_3^+ ion is given by Smyth, 1931.

H_3^+ ion Correction

In the past (A. O. Nier, 1947) the H_3^+ ion was corrected for by plotting the H/D ratio as a function of pressure of the gas in the source shield box and extrapolating to zero pressure. Since the concentration of H_3^+ is proportional to the square of the pressure (second-order reaction $H_2^+ + H = H_3^+$) and the HD^+ concentration is proportional to the pressure, the total mass-3 ion beam current will be:

$$I = ap + ap^2$$

If I is plotted vs. 1/p, a straight line whose $p = 0$ intercept will give the true HD^+ ion current should be obtained. Since at the low gas pressures that are used the H_2^+ ion current is proportional to pressure, one usually plots H_2^+ ion current vs. $H_2^+/H_3^+ + HD^+$ ion currents.

The establishing of this curve for each sample is time-consuming and the results are inaccurate; the mass spectrometer does not remain constant for the time necessary to make such determinations, the above curve is not linear, and the extrapolation to zero pressure is fairly large. Therefore, it was decided to minimize the H_3^+, to compare sample gas with a standard gas, and to keep the H_3^+ concentration constant in both gases during measurement.

The concentration of H_3^+ ions was minimized by working at low gas pressures, by adding the repeller electrode to the source, and by using as high an accelerating voltage as possible (2200 volts with an analyzer magnetic field strength of approximately 725 gausses; the high accelerating voltage also helped draw ions out of the source shield box and by so doing reduced the probability of the H_2^+ ion colliding with a neutral molecule in the shield box. The source magnet was adjusted for maximum electron-trap current (approximately 180–220 microamperes at a total filament emission of 3 ma) rather than for maximum ion current. The electron,

* Mark Ingram, personal communication.

accelerating and trap voltages were all adjusted for minimum H_3^+, as determined by the slope of the H/D ratio vs. H_2^+ beam intensity curve.

All the determinations were made at the same mass-2 ion current, 22·2 ± 0·2 volts across 1·5 × 10^{10} ohms. The repeller was then adjusted so that with the standard gas flowing into the source, the vibrating reed output was zero when the ratio dials read 00400, i.e., when the ratio, uncorrected for the difference in the resistance through which the two ion currents flowed, was 00400/111110 = HD/H_2.

The sample gas was then switched into the source by the use of solenoid-operated valves similar to those described by McKinney *et al*, 1950. The pressure of the sample gas was adjusted so that the mass-2 beam of the sample gas was

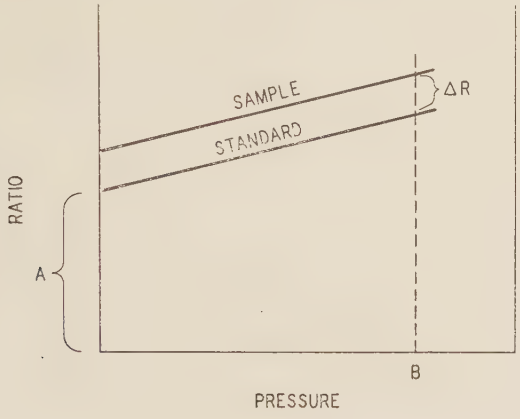

Fig. 1. Idealized plot of measured ratio HD/H_2 as a function of gas pressure in mass spectrometer ion source

equal to the mass-2 beam of the standard gas to within ±0·01 volts (1 part in 2220). The beam intensity of mass-2 was kept constant during the course of a determination by manually adjusting the pressure of both the sample and the standard gas. This adjustment presented no problem; it had to be attended to about every 3 to 5 minutes during a 20 minute run. In order to check the beam intensity to 1 part in 5000 it was necessary to have provision to buck out the voltage as indicated by the meter with a dry cell and Helipot potentiometer arrangement, so that the difference between the actual beam voltage and the bucking-voltage could be read on a sensitive voltmeter scale. The fluctuations of the beam voltage were in the neighbourhood of ±0·005 volts in a 22·2-v beam. At times it was possible to adjust the electronics so that the beam fluctuations over a period of 5 to 10 minutes were within the range ±0·002 volts in a 22·2-v beam. The method of comparison of sample gas with standard gas is described elsewhere (C. R. McKinney *et al*, 1950).

If no H_3^+ ion was present, the percentage difference between the ratio in the standard gas and the ratio in sample gas would be:

$$\frac{100 \times (\text{ratio dial reading for sample} - \text{ratio dial reading for standard})}{\text{Ratio dial reading for standard}}$$

The percentage difference between the ratios in the two gases corrected for H_3^+ ion is obtained as follows:

$$\frac{(\text{Ratio dial reading for sample} - \text{ratio dial reading for standard}) \times 100}{\text{Extrapolated reading for standard}}$$

This is shown in Fig. 1. In other words the difference ΔR (Fig. 1) at a large beam intensity is determined, and this reading is divided by the extrapolated dial

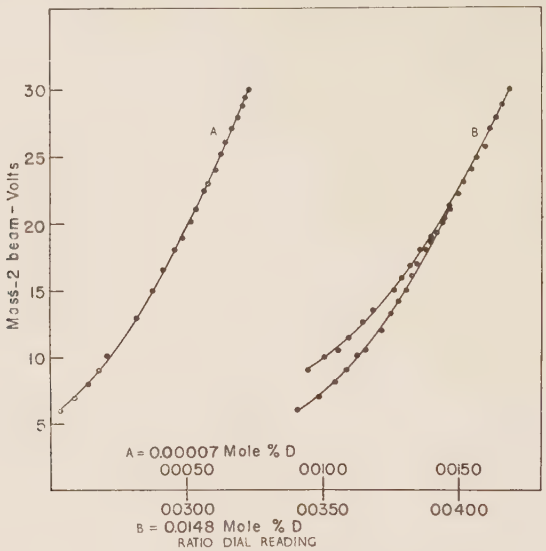

Fig. 2. Experimental plot of ratio dial reading vs. mass-2 beam intensity

reading for the standard gas. This method is applicable only to very pure H_2 gas, as impurities in the gas change the slope of the curve, so that the curves for standard gas and sample gas are no longer parallel.

This curve is not a straight line, but curves at low gas pressure. This indicates that the reactions

$$H_2^+ + H_2 \rightleftharpoons H_3^+ + H$$

$$H_2 \rightleftharpoons H + H$$

are becoming important, and act to lower the mass 2 ion beam current.

As a check on the H_3^+ correction, two samples of "light" water containing approximately 0·00007 mole % D were analyzed. The results are shown in Fig. 2.

The curves are essentially parallel to the curves obtained with the normal water which contains about 0·0148 mole % D. The lower part of the curves were not accurately determined, since the beam intensities are too low for accurate measurements. This, plus the curvature as mentioned above made it advisable in making the H_3^+ correction to extrapolate to zero pressure from the range 15 to 25 mass-2 volts. A calibration curve was plotted after each change to the instrument, such as the removal of the source or collectors.

Sample Preparation

The vacuum line used for the preparation of the hydrogen gas from water by the reduction with hot zinc is shown in Fig. 3. A 0·01-ml sample of water to be analyzed was drawn from a pipette into a thin glass capillary tube. The capillary tube was then sealed in a flame and placed in vessel *B*. An iron weight was placed in the vessel and held in place by an Alnico magnet, the assembly was connected to the vacuum line by means of a ground joint, and evacuated. The vessel was sparked with a Tesla coil to help remove adsorbed gas. When the pressure fell below 10^{-4}

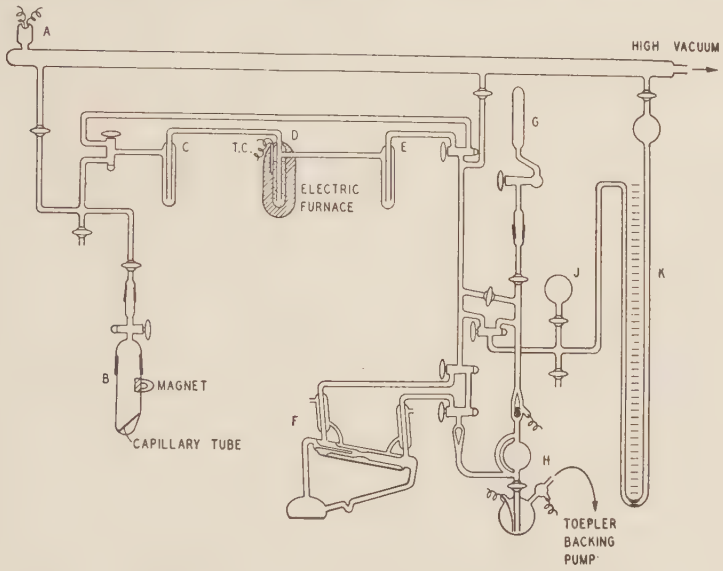

Fig. 3. Equipment used for the preparation of hydrogen gas from water samples

mm as determined by the thermocouple gauge. *A*, the system was isolated from the high-vacuum manifold, the trap *C* was cooled with liquid nitrogen, and the capillary tube broken by removing the magnet and allowing the iron weight to fall. Ten minutes was allowed for the water to be transferred to trap *C*. The system was then pumped to remove air that was held in the capillary tube. Trap *C* was allowed to warm up to room temperature while trap *E* was cooled with liquid nitrogen. The water vapour passed through trap *D*, which contained granulated zinc (about 30 grams of 10-mesh zinc) heated to about 400°C by the enclosing electric furnace. The zinc reacted with the water:

$$Zn + H_2O \rightleftharpoons H_2 + ZnO$$

producing hydrogen, which was pumped by means of the automatic Toepler pump *H* into the calibrated manometer *K*. When all the hydrogen was pumped into the manometer, the water that did not react and was condensed in trap *E* was made to travel back through the zinc in trap *D* by reversing the appropriate valves and warming *E* to room temperature while cooling *C* with liquid nitrogen.

It was found that 95 to 100% of the water reacted during the first pass over the

zinc if the zinc was hot enough. If the zinc was not hot enough, many passes were required and erratic results were obtained. After the hydrogen was measured, it was pumped into the sample tube *G*.

Care was taken to see that all the hydrogen was pumped into the tube during this transfer of the hydrogen, and during subsequent transfers, to minimize chances of isotopic fractionation.

With the line shown in Fig. 3 a sample could be analyzed completely in 45 to 70 minutes. The zinc trap *D* was replaced after approximately 100 runs, owing to the plugging of the trap by recrystallized zinc. All the water samples were analyzed in duplicate.

A sample of water from Lake Michigan was distilled and used as a working standard, and all the results in this paper are given in terms of this arbitrary standard.

The gas samples were placed on a vacuum manifold on the mass spectrometer and all of the gas was pumped into a reservoir behind the capillary leak, which has been described by Nier (1947). After a sample was mixed by alternate compressions and expansions, it was allowed to flow into the ion source via the capillary leak. The rate of flow of the hydrogen gas through the capillary leak into the source was about 0·05 standard cc per hour. During the course of a 10-hour day approximately 5% of the standard gas was passed through the leak. Apparently the rate of viscous flow in the forward direction through the capillary was not great enough to overcome the molecular flow in the backward direction. Therefore, a small amount of fractionation (approx. 0·05% per day) occurred and a correction had to be applied to the standard gas. This correction was determined by comparing the standard gas with two other samples of standard gas that were prepared by running triplicate samples of standard water through the line at the same time. The standard gas was replaced about every 4 to 7 days. Lengthening of the capillary tube as suggested by Halsted and Nier (1950) should reduce this fractionation effect and lengthen the period of usefulness of each standard.

The average error in a series of 86 analyses run in duplicate is $\pm 0{\cdot}066\%$ ($\pm 0{\cdot}0000098$ mole %).

Results—Water Samples

Several water sample analyses previously made by Kirschenbaum, Graff, and Forstat (1951) were checked. If the value of $0{\cdot}0147 \pm 0{\cdot}0001$ mole % D for Columbia University distilled water is accepted, our working standard is $0{\cdot}0148 \pm 0{\cdot}0001$ mole % D. With this value as a working standard, the results of the reanalyses are plotted against the data of Kirschenbaum, Graff, and Forstat (Fig. 4). The differences from their standard obviously differ from our results by a factor of two. As a check, the ratio of the vapour pressures of H_2O and HDO was determined at several temperatures. The results* agree with previous published work of Schultz and Zmachinsky† as well as with the calculated results of Wahl and Urey (1935).

* Samuel Epstein and Irving Friedman, in press.

† P. W. Schultz and W. C. Zamchinsky as reported by P. W. Schultz, SAM Report A–595, April 12, 1943, and W. C. Zamchinsky, unpublished report.

Table 1 lists the samples of natural water that were analyzed. All the results are accurate to $\pm 0{\cdot}1\%$. About half of the error is due to instrumental limitations and half to changes in the working standard and in the correction for H_3^+. The hydrogen results are given in terms of the percentage difference between the sample and the standard as regards the HD/H_2 ratio. Since the standard is $0{\cdot}0148 \pm 0{\cdot}0001$ mole % D, the conversion to mole % is given by:

$$0{\cdot}0148 + (\text{hydrogen results} \times 0{\cdot}0148) = \text{mole \% D in sample}$$

The oxygen results as determined by EPSTEIN (1953) are given in per mill (‰) difference in the $O^{16/18}$ ratio from the ratio in a standard CO_2 sample obtained from belemnites of the Peedee formation (Upper Cretaceous of North Carolina).

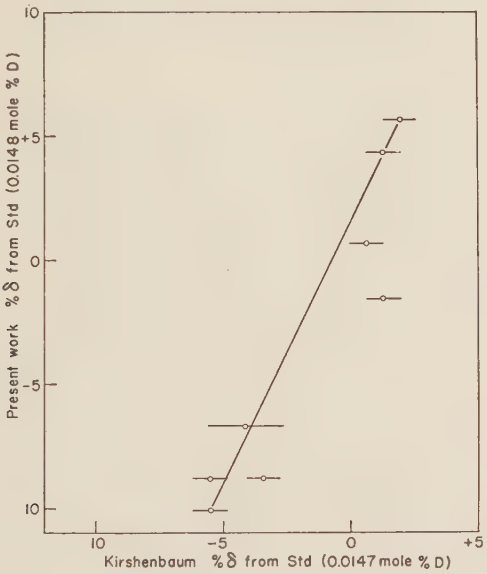

Fig. 4. A comparison of the results of the present research with the work of KIRSCHENBAUM *et al*

As most of the fractionation of hydrogen isotopes in the oceans is due to evaporation and condensation processes, the oxygen isotopes should be similarly separated; the ratio of the two fractionations should equal the ratio of the vapour pressures of H_2O/HDO and H_2O^{16}/H_2O^{18}. A plot both of the oxygen results as determined by EPSTEIN and MAYEDA (1953) and of the hydrogen results is given in Figs. 5. and 6 The slope of the line is approximately equal to the ratio of the vapour pressures at 30° to 40°C. The spread of the points, with the exception of the points from Great Salt Lake water, can be explained by the temperature effect.

The surface waters of the oceans have widely different isotopic compositions (see Fig. 5). In general equatorial waters are heavy, owing to the preferential loss of light hydrogen during evaporation and the concentration of the deuterium in the residue. This lighter water is deposited as rain at the higher latitudes,

Table 1. Water Samples

Ocean Water Samples

Station	Location		Depth Meters	Temperature °C	Hydrogen per cent*	Oxygen per mill*
	Lat.	Long.				
Albatross Expedition						
340 #19	S 00°13′	W 18°26′	25	22·6	+5·41	+0·48
340 #20	S 00°13′	W 18°26′	500	7·1	+4·75	−0·44
340 #21	S 00°13′	W 18°26′	2500	2·95	+4·95	−0·27
340 #22	S 00°13′	W 18°26′	7500	1·4	+4·63	−0·47
373 #23	N 28°05·	W 60°49′	25	28·5	+5·64	+0·95
373 #24	N 28°05′	W 60°49′	500	16·3	+5·45	+0·48
373 #25	N 28°05′	W 60°49′	2000	3·7	+5·09	−0·05
373 #26	N 28°05′	W 60°49′	6000	2·1	+4·97	−0·19
USS Serrano						
B 105	N 48°53′	W 135°00′	602	3·8	+4·77	−0·16
B 112	N 59°24′	W 144°50′	0	5·1	+3·66	−1·0
B 117	N 57°00′	W 150°00	110	4·7	+4·27	−0·20
A 228	N 28°18′	W 117°30′	0	16·8	+4·42	−0·43
A 257	N 25°42′	W 160°20′	0	24·4	+5·15	+0·23
C 532	N 43°58′	W 133°15′	0	15·5	+4·01	−0·98
J 100	N 26°18′	W 121°40′	0	21·5	+4·38	−0·53
J 276	N 33°19′	W 128°32′	294	7·8	+4·38	−0·20
J 331	N 35°41′	W 121°50′	0	12·3	+4·17	−0·80
Snellius Expedition						
1	N 47°53′	W 125°31′	10		+3·93	−0·65
4	N 4°52·7′	W 121°30·8′	1500		+4·55	+0·30
7	S 00°4·1′	E 79°43·2′	0		+5·15	+0·95
6	S 16°00′	E 94°56′	4000		+4·72	+0·14
9	N 11°00′	W 77°40′	800		+4·72	+0·25
15	N 36°38′	E 12°56′	0		+5·42	+1·38
19	Indian Ocean		0		+4·90	+0·45
Other Samples						
Jacksonville Beach, Fla., Sept. 1951			0		+5·02	+0·65
Middle Channel, Friday Harbor, Wash., July 25, 1949			225		+4·48	−0·62
Aquarium water, La Jolla, Calif.					+4·56	−0·45
Bermuda					+5·40	+1·09
President Channel, Friday Harbor, Wash., July 16, 1949			95		+3·25	−1·62
Between Morro and Encenada, Calif., Aug. 25, 1949					+4·30	−0·28
Bering Sea off Patterson Point, Little Sitkin Island, July 1950			0		+4·07	−0·81
	N 52°8′30″	W 176°54′	0		+4·17	−0·85
Off west coast of Greenland					−4·30	−11·10

*See paragraph 2 under "Results—Water Samples"

Table 1.—*continued*

Station	*Location*	*Depth Meters*	*Temperature °C*	*Hydrogen per cent**	*Oxygen per mill**
Other Samples (cont.)					
Off west coast of Greenland				+2·42	−3·35
Near Mount Pleasant Island, Maine Sample 1109		29		−4·19	1·12
Near Mount Pleasant Island, Maine Sample 168		29		+3·75	−1·15
Fresh Water Samples					
Snow, Chicago, Ill., 10 in. snowfall, Dec. 14, 1951				−8·28	17·0
Columbia River, Trail, B.C., July 17, 1943				10·1	17·24
Violin Lake, Trail, B.C., June 26, 1944				8·80	
Violin Lake, Trail, B.C., Nov. 6, 1943				8·83	
Violin Lake, Trail, B.C., Sept. 22, 1943				6·75	
Juneau Glacier, 235 ft below surface				−6·75	−12·75
Juneau Glacier, 155 ft below surface				6·75	−14·90
Grasshopper Glacier, Park County, Montana				10·61	
Great Salt Lake, Utah, Salt Lake boat harbor, Aug. 19, 1948				4·92	−7·43
Fumarole condensate from Paricutin, Jan. 1952				−0·85	+6·60
Spring water from Paricutin region, Jan. 1948				−2·37	
Rain water collected under Paricutin plume, 1947				0·98	
Standard water—Northwestern University, Dec. 17, 1942				−0·22	
Daisy Geyser, Yellowstone Park, Wyo.				10·03	
Punch Bowl, Yellowstone Park, Wyo				10·05	
Rain, Chicago, Ill., April 12, 1952				+0·89	−7·0
Gullmar Fjord, west coast of Sweden; collected April 29, 1952, by Nils Jerlov during plankton outburst				+2·13	−3·57
Mississippi River at Baton Rouge, La., May 3, 1948. Discharge about 450,000 cfs. U.S. Geol. Survey sample				+0·39	−4·90
Mississippi River at Clinton, Iowa, June 2, 1948. Discharge 29,700 cfs. Sample collected 5 ft below surface. U.S. Geological Survey				−1·63	
Platte River near Ashland, Nebr. May 7, 1948. Discharge 2,410 cfs. U.S. Geol. Survey sample				+0·87	
St. Lawrence River at Ogdensburg, N.Y., June 11, 1948				+0·66	
Susquehanna River at Marietta, Pa., May 29, 1948. Composite of 6 stations. U.S. Geol. Survey sample				−0·17	
Apalachicola River at Chattahoochee, Fla. Discharge 16,700 cfs. U.S. Geol. Survey sample				−4·23	
Sacramento River at Verona, Calif. Discharge 14,900 cfs. U.S. Geol. Survey sample				1·41	
San Joaquin River near Vernalis, Calif., July 7, 1948. Flow 1,800 cfs. U.S. Geol. Survey sample				2·29	
Connecticut River at Thompsonville, Conn., June 17, 1948. Flow 20,640 cfs. U.S. Geol. Survey sample				−2·15	
Ohio River at Louisville, Ky., June 4, 1948. Flow 42,000 cfs. U.S. Geol. Survey sample				+0·19	
Arkansas River at Van Buren, Ark., June 3, 1948. Flow 18,000 cfs. U.S. Geol. Survey sample				−3·25	

*See paragraph 2 under "Results—Water Samples"

Table 1.—*continued*

Station	*Location*	*Hydrogen per cent**	*Oxygen per mill**
Fresh Water Samples (cont.)			
Rio Grande River near Mission, Tex., April 1–30, 1948. U.S. Geol. Survey sample		+3·28	
Missouri River at Kansas City, Mo., June 12, 1948. Discharge 73,000 cfs. U.S. Geol. Survey sample		−7·06	
Red River at Denison Dam near Colbert, Okla., Mar. 8–11, 14–20, 22–31; April 1–9, 11–21, 23, 25, 29–30, 1948		+3·05	
Red River of the North at Oslo, Minn., July 12, 1948. Discharge 1,750 cfs. U.S. Geol. Survey sample		−0·06	
Colorado River at Yuma, Ariz., June 4, 1948. Discharge 8,420 cfs. U.S. Geol. Survey sample		−6·06	
Snake River near Clarkston, Washington. U.S. Geol. Survey sample		−5·77	
Roanoke River near Scotland Neck, N.C., June 17, 1948. Discharge 6,500 cfs. U.S. Geol. Survey sample		+1·62	
Bermuda rain, thunderstorm, June 27, 1949		+0·53	−6·55
Monongahela River, near Morgantown, W. Va., March 26, 1943		−1·62	−9·10

making high-latitude water light. Note the analysis of Bermuda rain: +0·53‰ whereas surface water is +5·40‰. The Bermuda rain was collected during a very heavy downpour; we can assumed that most of the water in the cloud was deposited, and that in composition the rain is a fairly good sample of the average composition of the vapour over the ocean in that region.

Epstein and Mayeda (1953) first noted that, although the surface waters of the oceans varied greatly in their oxygen isotopic composition, deep waters all tended to be light. A check of the relation between hydrogen isotopic composition and depth at two widely separated spots in the Atlantic (Albatross expedition samples) shows that the hydrogen isotopes also show this trend. As pointed out by Epstein and Mayeda, this trend may prove that polar bottom currents penetrate as far as the equator.

Chicago rain, from a large warm tropical Atlantic and Gulf of Mexico air mass, analyzed +0·89. Here also, most of the moisture in the cloud was deposited, as a 3-day rain occurred at the static juncture of a cold air mass with the warm moist tropical Gulf air. In composition, this represents a good sample of the vapour above the Gulf of Mexico region. Since much of the Great Lakes drainage rainfall is of the same origin, it is not surprising that the Great Lakes water shows about the same percentage as the rain sample. The fact that the Great Lakes water is about 1‰ lighter in its hydrogen deuterium ratio than the rain sample can be explained by the fact that some of the lake water originates from winter snow, which is quite light (Chicago snow −8·28‰). This snow is derived from Pacific Ocean moisture that had passed over several mountain ranges and had deposited much of its moisture before arriving in the mid-west region. The explanation given

by KIRSCHENBAUM (1951) for the lightness of Trail, British Columbia, water would also apply here.

"It is not unreasonable to expect that fractionation may occur as precipitation of water vapour from the air occurs. The first fraction precipitating may be higher in deuterium owing to the difference in vapour pressure of H_2O and HDO. Therefore as the winds rise to go over the mountains and much precipitation takes place, the effect may be that of Raleigh distillation in reverse, with the residual water having low deuterium content. Thus, on the basis of this hypothesis, the winds reaching the vicinity of Trail contain water somewhat depleted in deuterium. Consequently the waters which receive the last rains from these winds have a low deuterium content."

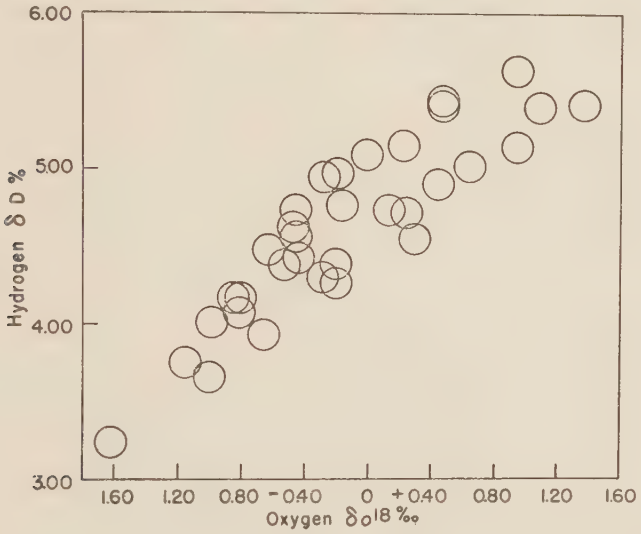

Fig. 5. A plot of the O^{16}/O^{18} and H/D results on samples of ocean water

Rivers on the Pacific coast that drain the western slope of the coast range are fairly heavy—Sacramento River −1·41%; San Joaquin River −2·29%. The same is true of east coast rivers that receive Atlantic Ocean air—Connecticut River −2·15%; Susquehanna River −0·17%. Rivers that receive Gulf air will all be of a composition close to that of Chicago rain, since there is no mountain barrier to remove much of the water before the Gulf air deposits its water in the Central Great Plains area—note the Platte River +0·87% and the Ohio River +0·19%, and the Mississippi at Baton Rouge +0·39%. Rivers draining the upper Plains States and the Rocky Mountain region receive much Pacific water as winter snow, and therefore they are light: for example, the Columbia River at Trail, British Columbia −10·1%. The Missouri River at Kansas City (−7·06%) has been somewhat diluted on its way south. The Mississippi River at Clinton, Iowa—mostly Gulf rain with some admixture of Pacific snow—is −1·63%. The Colorado River at Yuma, Arizona (−6·06%) and the Snake River at Clarkston, Wash.

(−5·77‰), drain areas of high summer evaporation; which tends to make them heavier than the snow in the region (approx. −10‰). Evaporation also accounts for the compositions of the Rio Grande +3·28‰, the Red River of Oklahoma +3·05‰, and the Arkansas River +3·25‰. If we assume that the rainfall source water is about +0·5‰ and that the evaporation takes place at 50°C, the fractionation during evaporation will be 5‰, and about two-thirds of the water would have to evaporate to yield a residue as heavy as +3·25‰. The Apalachicola River of Florida yielded the heaviest river water that we determined (+4·23‰); and, here too, high re-evaporation of the source water is the probable explanation.

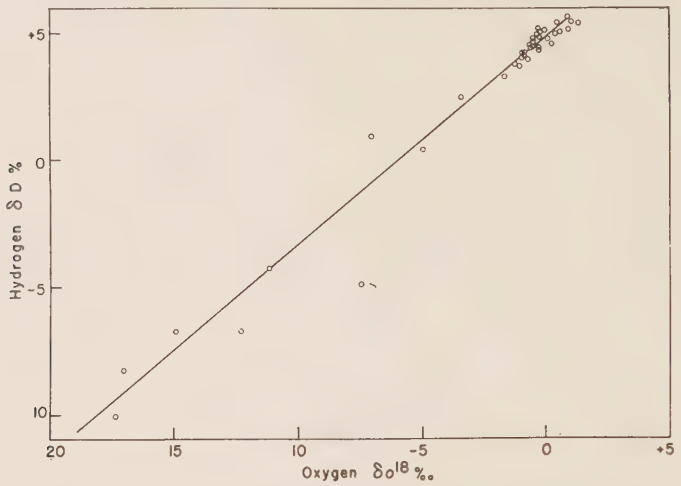

Fig. 6. A plot of O^{16}/O^{18} and H/D results on samples of ocean and fresh waters. The closely spaced group of points in the upper section of the graph represent sea water samples, and are plotted separately in Fig. 5

These samples of river water were, with a few exceptions, single samples collected during a period of a few minutes, they may have been contaminated by nearby springs or tributaries, as well as by recent rain. Therefore the conclusions drawn from the analyses of these samples must be treated as preliminary in nature.

Several melted core samples from the Juneau ice cap, Juneau, Alaska, were analyzed. The hydrogen results show no difference between the 155-ft level and the 235-ft level. The oxygen results differ greatly. This may be a case of the hydrogen ion diffusing through an immobile oxygen lattice.

The apparent seasonal variation in Violin Lake, at Trail, B.C., can be explained by summer evaporation concentrating the heavy isotope in the residue.

Miscellaneous Results

The sample of fumarole condensate from Paricutin is interesting. It is approximately 1·5‰ heavier in hydrogen isotopic composition than spring water from the region, a fact in itself not significant. However, the oxygen isotopic content of +6·6‰ indicates that the oxygen in the water equilibrated with the oxygen in the

silicate rocks of the region; the rocks, according to SILVERMAN (1951) analyze +6·0‰. This equilibration must have taken place at a relatively high temperature.

Two Yellowstone Park geysers agree closely at −10·0‰, a value that is probably close to the composition of the ground water and snow of the region. Samples of gas from several fumaroles in Yellowstone Park give very low results—approximately −20‰ (Table 2). These samples were collected by H. CRAIG and represent the hydrogen from both methane and free hydrogen in the gas. One sample from a spring issuing from Hurricane Vent, Norris Geyser Basin, showed

Table 2. Yellowstone Park Gas Samples Collected August 1950

Name	*Location*	*Hydrogen per cent**
Spring issuing from Hurricane Vent, Norris Basin		−46·3
Daisy Geyser, Upper Basin		−23·1
Punch Bowl Spring, Upper Basin		−19·2
Iron Creek, pool on bank 75 ft north of footbridge, between bridge and Cliff Geyser on west side of creek		−19·2
Kaleidoscope Group, Lower Basin. Small spring 30 ft from Kaleidoscope Geyser		−19·3

* See paragraph 2 under "Results—Water Samples"

−46·3‰. According to DAY and ALLEN (1935) the gas from this spring contains 0·50% H_2 and 0·20% CH_4, the same authors claim that the other spring gases analyzed contain 0·00% H_2.

If we assume that these gases from all the springs were equilibrated at the same temperature, and subtract the methane hydrogen from the "Hurricane Vent" analysis, the hydrogen portion would give a minimum temperature of 400°C for the reaction $H_2 + HDO \rightleftharpoons HD + H_2O$ [Data from SUESS (1949)]. This conclusion is in essential agreement with the findings of BOATO and CARERI, 1952. More gases remain to be collected and separated before minimum temperatures can be assigned to these igneous activities.

In order to check the hydrogen isotopic relationship of the organic matter and the sea water in which an organism grows, two samples of abalone shell containing organic matter were run. The coarsely ground shell was mixed with powdered copper oxide previously treated with purified oxygen at 900°C; the mixture was degassed at 100°C and then heated to 800°C. The water produced by the combustion of the organic matter was processed in the usual way. The isotopic composition of the organic hydrogen was −4·5‰ whereas the composition of the ocean water in contact with the living organism was +4·5‰. Apparently the organism fractionates its hydrogen by a large factor.

In this connection an interesting problem would be the separation and analysis of the different constituents of the organic matter in a manner that would not alter their hydrogen isotopic compositions. The problem of bound and free water in colloid systems complicates the situation.

An attempt was made to separate and analyze the hydrogen contained in an iron meteorite. As a check on the temperature necessary to remove water from the hydrated iron oxide that both coats and permeates most iron meteorite samples, a 3·5-g sample of surface scale from the Canyon Diablo meteorite was chipped off for analysis. This sample was heated in a vacuum and the evolved water collected, measured, and analyzed. Table 3 lists the results.

Table 3. Canyon Diablo meteorite

Temperature °C	*Time of heating* Hours	*Amount of water evolved, milligrams*	*Analysis of water* % *of hydrogen**
20	12		
125	2	10	— 5·0
235	4	100	−10·5 ± 2·5
375	6	30	−11·0 ± 3
510	1	5	

* See paragraph 2 under "Results—Water Samples"

Apparently the oxide holds its water tenaciously. Heating to too high a temperature in an attempt to remove this terrestrial water causes loss of dissolved hydrogen by diffusion, as the following experiment shows.

A 10-g sample of chips of "fresh" Canyon Diablo meteorite was heated in a vacuum at 75°C, for 10 hours and at 125°C for another 10 hours. It was then heated at 450°C for 2 hours and the 10 mg of water was collected in a dry-ice trap. This fraction analyzed −9·4%. The chips were then burned in purified oxygen at 1200°C forming 0·5 mg of water, which analyzed +11·7%. Apparently while heating at 450°C hydrogen was lost by diffusion, and the deuterium was concentrated in the residue. A sample of hot-rolled iron treated in the same manner as the above meteorite sample gave essentially the same results.

In addition to loss of hydrogen by diffusion there is also the danger of contamination by exchange with hydrogen produced by the reaction of the iron with the absorbed terrestrial water during the degassing of the meteorite chips.

In view of the above results, great care must be exercised in interpreting hydrogen analysis of iron meteorites.

Acknowledgments—I would like to acknowledge the aid and encouragement of HAROLD C. UREY, who suggested the problem and who contributed greatly at every point.

I would also like to thank SAMUEL EPSTEIN and T. MAYEDA for their co-operation in making available to me hitherto unpublished figures on the oxygen isotopic analyses of the waters listed in Table I.

Thanks are also due to RICHARD BADER, HARMON CRAIG, FARRINGTON DANIELS, H. PETTERSSON, and JEROME WASSERBURG for furnishing me with samples, and to HAROLD ALLEN, DAVID LEE, and JOHN GODFREY for their assistance.

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Book review

PORTER, J. G.; **Comets and Meteor Streams.** Chapman and Hall, Ltd., London, 1952. 28/-.

"The conclusion is inevitable that all meteors, like comets, are members of the solar system." With these words the author summarizes his comprehensive discussion of the information available to-day. One would imagine him to do it with justifiable pride, for he unwaveringly defended this view at a time when, by HOFFMEISTER on the Continent of Europe, and by ÖPIK in U.S.A. and Estonia, the interstellar origin of the vast majority of meteors was proclaimed with the greatest confidence. Moreover, based on an extrapolation from his studies on large meteors, and on very few and doubtful observations on meteorites, HOFFMEISTER had declared it a "well established fact," that meteorites too are of interstellar origin; his reputation as an authority was great enough to hinder, by this statement, the recognition of the true nature of meteorites for a considerable time.

Some of the most convincing proofs that HOFFMEISTER's views were untenable has been provided in recent years by radar observations on meteors. Together with equally unambiguous photographic measurements of meteor velocities they ought now to convince every unbiased person that the author's statement quoted above can no longer be disputed. Only as an instance of the tenacity with which some scientists cling to their favourite ideas, we should like to mention that in the volume *Astronomie und Geophysik* of the well-known LANDOLT-BÖRNSTEIN tables, in the chapter on meteors, the interstellar meteor streams are still defended. This volume was published in 1952; the author of the chapter on meteors is HOFFMEISTER.

With its many tables, complete derivation of mathematical formulae, and advice for practical computation, Dr. PORTER's book is in the first place meant for the use of professional astronomers; but as comets and meteors are among the most spectacular sights of the night sky no doubt a considerable number of amateurs in astronomy will be interested in this very competent and up-to-date report.

F. A. PANETH.

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